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LIV.—THE RELATIVE VALUES OF THE ATOMIC WEIGHTS OF HYDROGEN AND OXYGEN.¹

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INTRODUCTION.

Since the application by Dalton of the atomic theory to explain the definiteness of the combining proportions of the elementary substances of chemistry, these proportions have been generally regarded as the ratios of the weights of the atoms, and the values assigned to each element have been generally called atomic weights.

The conception was early suggested and advocated by Dr. Prout, an eminent physician of London during the first half of this century; that the elementary atoms were all aggregates of the atom of hydrogen, the lightest atom known. If this were true, it would of course follow that the atomic weights of the elements would all be multiples of the atomic weight of hydrogen; so that, if the weight of the atom of hydrogen were selected as the unit of the system, all other atomic weights must be multiples of this unit, and therefore whole numbers.

The facts known at the time (1815) were not inconsistent with this view; but as the methods of chemical analysis were improved,

¹ Proceedings of the American Academy of Arts and Sciences.

and the combining proportions determined with greater accuracy, marked discrepancies from Prout's hypothesis appeared. Still, so great was the hold which the conception had taken upon chemical students, that for a long time the nearest whole numbers to the combining proportions observed were accredited as the true value of the atomic weights, rather than the actual mean of the experimental results; and this practice is still followed in many standard publications, notably the "*Jahresbericht über die Fortschritte der Chemie.*" In many cases the observed values were so near whole numbers that no important error in the calculation of analyses arose from this practice, the differences neglected being no greater than the uncertainties of analytical method, and this was especially true with regard to the larger atomic weights.

One exception to the theory, however, was so marked that it could not be overlooked, namely, the atomic weight of chlorine, which was capable of being determined with great accuracy; and all the determinations uniformly gave a result which was closely 35.5. This and a few similar cases suggested the idea that, if the atomic weights were not even multiples of the received hydrogen atom, they might be multiples of the half or quarter hydrogen atom, which would simply amount to taking as the ultimate atom of material things a still smaller unit.

The well known chemist, Dumas of Paris, was led by this view to undertake a redetermination of a large number of atomic weights, and many of the results then obtained are still accepted as authoritative.¹ As was to be expected, Dumas found a much closer agreement with this modified theory than with the original hypothesis of Prout; but obviously such evidence could have but little bearing on the general theory that the atoms were all aggregates of some common unit, for by taking that unit small enough—even no smaller than the one hundredth of the received hydrogen atom—all the atomic weights, even those most accurately determined, would be expressed by whole numbers within the limits of probable error.

Soon after, Stas of Brussels, a former assistant of Dumas, endeavored to set the question of Prout's theory at rest by an investigation which will be ever memorable for its extreme accuracy.² He selected for his investigation those elements whose

¹ *Ann. chim. phys.*, 3d ser. **55**, 129 (1859).

² *Mémoires de l'Académie Royale de Belgique*, **35**. Also *Ann. Chem.*, (Liebig), Suppl. **4**, 168.

combining proportions were capable of being determined with the greatest accuracy, and, working on large quantities of material, with every refinement which a full knowledge of analytical methods could suggest, he obtained results which it seemed impossible to reconcile with the theory in any way. This investigation, published in 1865, seemed at first to disprove the theory altogether.

Nevertheless, when Stas's results came to be collated, and as other determinations of similar accuracy came to be published, the fact appeared that a large number of the most accurately determined atomic weights stood to each other in the relation of whole numbers within the limits of accuracy of the most refined experimental work. The number of these cases was so large that it seemed highly improbable that the coincidences should be the result of chance.

This idea was prominently set forth by Professor Mallet of the University of Virginia, in his admirable paper on the Atomic Weight of Aluminum,¹ which was a striking illustration in point; and the same feature was also made prominent by Professor F. W. Clarke of Washington, after a careful review of all the determinations of atomic weights.²

The coincidences appear more striking if the values of the weights referred to are given in values of the oxygen atom assumed to be 16, as has been done by Professor George F. Becker in his digest of atomic weight determinations.³ The following table from the writer's work on Chemical Philosophy will make clear the point in question.

Atomic Weights most Accurately Determined.

Hydrogen	1.002	Chlorine	35.46
Lithium	7.01	Potassium	39.14
Carbon	12.00	Calcium	40.00
Nitrogen	14.04	Bromine	79.94
Oxygen	16.00	Silver	107.93
Aluminum	27.02	Antimony	119.92
Sodium	23.05	Iodine	126.85
Magnesium	24.00	Barium	137.14
Phosphorus	31.05	Thallium	204.11
Sulphur	32.07	Lead	206.91

¹ Phil. Trans. 1880, p. 1003.

² Smithsonian. Misc. Coll.; Constants of Nature, Part V, p. 270.

³ Ibid. Part IV.

This table includes all the atomic weights which up to 1882 could be regarded as known within one thousandth of their value, and with one or two notable exceptions there is no instance in which the value differs from a whole number by a quantity greater than the possible error, though not always the "probable error," of the processes employed in their determination.

Were these numbers wholly independent of each other and distributed by no law, we should expect to find every possible intermediate value, and the fact that they so nearly approach whole numbers cannot fail to produce on the mind the impression that there is some influence which tends to bring about this result.

It may be that the discrepancies are due to unknown constant errors, which every experimentalist knows are greatly to be feared. Or it may be that there is in nature a tendency to whole multiples; and this last view, if not compatible with our present conception of the atomic theory, may hereafter appear as one of the phases of a broader philosophy.

The force of evidence which such a distribution of values as the above table presents was brought home to the writer in his investigation of the atomic weight of antimony.¹ After eliminating various causes of error, he was enabled to determine with great accuracy the atomic weights of antimony, silver, and bromine, in one and the same series of experiments; and it appeared that this ratio was

$$120.00 : 108.00 : 80.00,$$

with a probable error of less than one in the last decimal place. Here then is a ratio of whole numbers within the one hundredth of a single unit. Since the ratio of the atomic weights of silver and oxygen has been determined with great accuracy, we can extend the above proportion to a fourth term, the atomic weight of oxygen, which appears also as a whole number, perhaps with a somewhat larger probable error. Still, we have not reached the unit of the system, and when we attempt to extend the ratio to the atomic weight of hydrogen, we find that the most probable value from all experiments hitherto made gives the ratio not of 16 to 1, but of 16 to 1.0025.

If now we wished to refer to the hydrogen unit the atomic weights of antimony, silver, bromine, and oxygen, whose ratios of

¹ Additional Experiments on the Atomic Weight of Antimony, *Am. Acad. Proc.* 17, p. 13, by Josiah Parsons Cooke.

whole numbers had been determined as above, it was only necessary to divide all the terms of the above proportion by 1.0031, when we obtain the series of values given below the others, and all semblance to the hypothesis of Prout disappears, although of course the second series of numbers bear the same ratios to each other as the first :

Antimony.	Silver.	Bromine.	Oxygen.	Hydrogen.
120.00	108.00	80.00	16.01	1.0031
119.60	107.66	79.75	15.96	1.00

The numbers in the lower of the two proportions appear as uncommensurable as Stas maintained that they were, and the same is true of most of the atomic weights, when given, as is usual in recent text-books, on the basis of the hydrogen unit.

When as the result of his investigation on the atomic weight of antimony there was presented to the writer the ratios of whole numbers as shown in the first of the above proportions, with the single exception of the atomic weight of hydrogen, the question was at once suggested : Is the ratio of the atomic weights of oxygen and hydrogen in fact that of 16 : 1.0025, as the general average of all trustworthy determinations hitherto made seems to indicate, or was there some constant error lurking in these results which caused the very slight variation from 16 to 1 required by the theory? In looking at the proportion thus displayed, it seemed as if the variation from the theory must be apparent, and he determined to ferret out the hidden error if possible. This investigation was undertaken in the autumn of 1883, but owing to the condition of the writer's sight the work has been greatly delayed.

No one can study the record of the investigations by which the ratio of the weights of the oxygen and hydrogen atoms has been determined, without receiving the impression that they are by no means decisive in regard to the theory we are discussing, and it is also equally evident that this ratio, if it could be fixed beyond doubt, would be a crucial test of the theory.

Previous Work.

The methods by which the atomic weights of oxygen and hydrogen have been determined may be divided into two classes : first, the direct method of determining the ratio in which the proportions of oxygen and hydrogen uniting to form water were actually

weighed; secondly, the confirmatory method, to whose results small weight could be given independent of the first.

Among confirmatory methods we must unquestionably class the classical determinations by Regnault of the density of oxygen and hydrogen gases under normal conditions at Paris; that is, in so far as these determinations bear on the question of the ratio of the atomic weights.

According to the molecular theory the ratio of the densities of oxygen and hydrogen gases could only be the ratio of their molecular or of their atomic weights when both materials were in the condition of perfect gases, of which condition the test would be an exact conformity to Mariotte's law. Now, as Regnault himself elegantly demonstrated, oxygen and hydrogen gases at the standard conditions of temperature and pressure not only do not exactly obey Mariotte's law, but the deviations from the law in these two cases are in the opposite directions, oxygen gas being condensed by increasing pressure more, and hydrogen gas less, than the law requires. Hence theory would not lead us to expect that the ratio of the densities of these gases at the standard conditions would be the exact ratio of their atomic weights. But obviously it may be that this inference from the molecular theory is not legitimate, or it may be that the effect of the imperfect aeriform condition would not perceptibly influence the apparent atomic ratio; and hence the confirmation afforded by Regnault's results is of value.

In the same category we must class also the determination of the atomic weight of oxygen made by Thomsen of Copenhagen, who weighed the amount of water obtained by burning a measured volume of hydrogen gas. Here the reduction of the volume to weight involved a knowledge of values and conditions which could not be known with the greatest accuracy, and unfortunately the details of the experiments have not been published.

Again, we should class simply as confirmatory results deduced indirectly, and involving the values of other atomic weights, however accurately these subsidiary values may be supposed to be known; such, for example, as Stas's determination of the amount of chlorine in ammoniac chloride.

Turning now to the actual direct determinations of the combining proportions of oxygen and hydrogen, there are only two which are of any present value. Of these by far the most important is the classical investigation of Dumas, "*Researches on the Composition*

of Water.” This is one of the most memorable investigations in the history of chemistry, and its general principles are known to every student of the science. An indefinite amount of hydrogen was burnt by means of cupric oxide; the amount of oxygen consumed was determined by the loss of weight of the combustion tube, and the amount of water formed was collected and weighed directly. The experiments were on a very large scale, the amount of water produced varying from 15 to 70 grams. The greatest care was taken to insure the purity of the materials used, every known experimental means was employed to secure accuracy, and all necessary corrections were applied to the results. Estimated on the system at present in use, the value of the atomic weight of oxygen obtained by Dumas as the mean of nineteen determinations was 15.9607, with a probable error of ± 0.0070 , the highest value being 16.024, and the lowest 15.892.

The investigation of Erdmann and Marchand² was far less extended, and some of the precautions taken by Dumas were neglected because deemed unnecessary. No pains seem to have been taken to obtain pure cupric oxide, and the material used in several of the determinations was described as “kaufliche Kupferglühspan,” while that used in the others was obtained by igniting cupric nitrate; and no proof is adduced in either case of the purity of the material employed.

The results are divided into two groups, and in the experiments of the second group the air was exhausted from the combustion tube before weighing; but it appears from the paper that the marked difference between the two series of experiments depended rather on the character of the cupric oxide, and on varying conditions used, than on this circumstance. The first series of four results, when averaged, gave the value 15.937, with a probable error of ± 0.0138 , while the mean of the second series was 16.009, with a probable error of ± 0.0030 . The study of the paper, however, does not confirm the expectation that the results of the second series are more trustworthy; for the closer agreement and smaller probable error appear to be the result of the identity of conditions, which was maintained in this series, but not in the first. Judging from the paper, we should be inclined to place most reliance on the first series, in which the conditions of the experiments were varied, rather than on the second, which seems obviously to be influenced by some constant error.

¹Ann. chim. phys., 3d ser. 8, 189 (1842).

²J. prakt. Chem. 1842, 26, 461.

The results, then, thus far obtained, are as follows :

Direct Determinations.

Dumas (nineteen determinations)	15.9607 ± 0.0070
Erdmann and Marchand (first four)	15.9369 ± 0.0138
“ “ “ (second four)	16.0095 ± 0.0030

Confirmatory Determinations.

Dumas and Boussingault ¹ (gas densities)	15.954 ± 0.031
Regnault ² (gas densities)	15.961 ± 0.0044
Thomsen ³ (not fully described)	15.960

The one process by which the relative combining proportions of oxygen and hydrogen have been hitherto directly determined is open to serious criticism. In the first place, the circumstance that the weight of the hydrogen is eight times smaller than that of the oxygen, and that this weight has only been estimated by difference, is exceedingly unfavorable to the accuracy of the process. It can easily be seen that, in order to establish a ratio like 1 to 8, the highest accuracy demands that each term of the proportion should be known to an equal degree of exactness. Thus if in a given experiment we have 8 grams of oxygen uniting with 1 gram of hydrogen, it is of no avail to weigh the oxygen to the tenth of a milligram, unless we can weigh the hydrogen to the same proportionate degree of accuracy. For an error of eight tenths of a milligram in the weight of the oxygen, or an error of nine tenths of a milligram in the weight of the water, will have no more influence on the ratio we are seeking than an error of one tenth of a milligram in the weight of the hydrogen. Now, in the process we are discussing the weight of the water can be determined to within a few tenths of a milligram; that is, with all the accuracy with which our problem requires that the larger term of the proportion 8 to 1 should be known. It is quite different with the weight of the oxygen. This last is found by weighing the glass combustion tube containing cupric oxide before and after the experiment, and between the two weighings the tube is heated to a low red heat for several hours while a stream of hydrogen gas is passing through it; and there are several causes which may lead

¹ Compt. rend. **12**, 1005; also Constants of Nature, Part V, p. 6.

² Compt. rend. **20**, 975; also Constants of Nature, Part V, p. 6.

³ Ber. d. chem. Ges. **3** (1870), 928; also Constants of Nature, Part V, p. 8.

to the variation of these weights, independent of the oxygen which has been used up in the process. We shall allude to some of these causes below, but their effect would be comparatively unimportant if they only led to a small error in the observed weight of the oxygen. Unfortunately their effect is not thus limited; for when, in order to find the weight of the hydrogen, we subtract from the weight of the water, which may be regarded relatively as accurately known, the weight of the oxygen, which may be for the causes referred to slightly erroneous, the whole error appears in the weight of the hydrogen thus found, and in the opposite direction. If, for example, the weight of the oxygen is too large, the weight of the hydrogen will be too small by exactly the same amount; and although the error may be an inconsiderable part of the weight of the oxygen, it may be a very appreciable quantity in the weight of the hydrogen.

On the other hand, if a means could be devised for weighing the hydrogen, leaving the oxygen to be determined by subtracting this smaller weight from the weight of the water, then a small error in the observed weight of the hydrogen would have no appreciable effect on the weight of the oxygen.

Dumas fully recognised the source of error to which we have referred, and in his paper on the subject wrote what may be translated as follows:

"Of all analyses presented to a chemist, that of water is the one which offers the greatest uncertainty. Indeed, one part of hydrogen unites with eight parts of oxygen to form water, and nothing would be more exact than the analysis of water if we could weigh the hydrogen as well as the water which results from its combustion. But the experiment is not possible under this form. We are obliged to weigh the water formed, and the oxygen which was consumed in producing it, and to determine by difference the weight of the hydrogen which has entered into combination. Thus an error of $\frac{1}{800}$ in the weight of the water, or of $\frac{1}{800}$ in the weight of the oxygen, is equivalent to an error of $\frac{1}{80}$ or $\frac{1}{90}$ in the weight of the hydrogen. Let these two errors be in the same direction and the total error will amount to $\frac{1}{40}$."

In the second place, however carefully the exterior surface of the combustion tube may be guarded, it is impossible that the contents of the tube should bear the same relations to the surrounding atmosphere before and after the combustion. We begin with a tube

containing cupric oxide in different states, and we end with it containing reduced copper, whose condition will vary more or less with the character of the oxide employed; and the power of these materials to occlude air or hydrogen is an unknown quantity in our experiment. That it is an appreciable quantity is evident from several incidental observations.

Dumas endeavored to avoid any source of error arising from this cause by exhausting the combustion tube before weighing it, but he himself expresses a doubt whether a trace of hydrogen might not have been left. Erdmann and Marchand in part of their experiments resorted to the same expedient, but their results obviously vary with the condition of the cupric oxide employed; and the following remarks of Schutzenberger, in a discussion of the variability of the law of definite proportions before the Chemical Society of Paris in 1883, as quoted in the "American Journal of Science," 3d series, Vol. XXVI, page 65, have an important bearing on the same point:

"When water is synthesised by reduction of a known weight of CuO , by weighing the reduced Cu and the water formed, it is found that the ratio of O to H is not constant, but varies with the state of division and of saturation of the oxide, the duration of contact of the water formed with the oxide, and with the temperature, from 7.95 to 8.15. The latter value is obtained with a saturated and divided oxide filling the tube, the former with oxide in lumps filling the tube for a space of 25 cm. With a larger empty space the ratio has fallen to 7.90. When the synthesis of water is effected by weighing the hydrogen consumed (as by dissolving a known weight of zinc in HCl) and the water formed, the ratio differs according to the contents of the combustion tubes. If it contains granular CuO of a length of 80 cm. heated to redness, the ratio $\text{O} : \text{H}$ is 7.96 to 7.98 to 1; at a low temperature, 7.90 to 7.93; if the CuO is replaced by PbCrO_4 , from 7.89 to 7.93."

In addition to all this, impurities in the oxide of copper might have a serious influence on the result. As before said, Erdmann and Marchand speak of using "kaufliche Kupferglühspan"; but in our work we could find no commercial cupric oxide which did not contain a marked amount of arsenic. We examined a number of specimens coming from the best German and American dealers, and there was not a single instance in which we did not find arsenic, and even when the material was marked "purissimum." In some

cases the amount of arsenic was so great that, after successive reductions and oxidations, abundant crystals of arsenious oxide collected at the exit end of the combustion tube. It is unnecessary to add that the hydrogen used was free from all such impurity.

For our own experiments, of which the results are given below, not only was the oxide of copper prepared from absolutely pure electrolytic copper, but also, as will be shown, the combustion tube was left at the end of the determination as it was at first, and the same tube was used for a number of experiments.

Apparatus for weighing Hydrogen.

In entering on a new investigation of the oxygen and hydrogen ratio, it was evident at the outset that no advantage was to be gained by multiplying determinations by the old method. The only hope of improvement lay in finding some method of weighing the hydrogen with sufficient accuracy; and it was essential to determine this weight to within one ten-thousandth, or at least one five-thousandth, of its value.

A gas can only be weighed by enclosing it in a glass globe, or some similar receiver, and hydrogen is so exceedingly light that its total weight can only be a very small fraction of the weight of the containing vessel. Moreover, as the buoyancy of the air is fourteen and one half times as great as the weight of the hydrogen, the variations in buoyancy caused by changing atmospheric conditions have an all-important effect on the apparent weight. The late Professor Regnault, of Paris, devised, however, a very ingenious method of compensation, which could readily be applied in this case. It consisted in balancing the globe containing hydrogen, hung to one arm of the balance, by a second globe of exactly the same external volume and made of the same material, hung to the opposite arm; and so arranging the balance case that they should hang in the same enclosure, and therefore be equally affected by atmospheric changes. This method was applied in the problem before us; and after a number of trials it was found possible to make the compensation so accurate that under good conditions the weight of a globe holding five litres of gas did not vary more than one tenth of a milligram through large changes of temperature and pressure. In order now to weigh hydrogen with this apparatus, it was only necessary to exhaust the air from the glass receiver, and, after balancing it as described, to fill it with

pure gas, when the increased weight—less than half a gram with our apparatus—was the weight of hydrogen required.

The balance employed was an excellent one, made about twenty years ago by Becker and Sons, of New York. With a load of five hundred grams in each pan, it turns very perceptibly with one tenth of a milligram, and shows this small difference of weight with very great constancy.

The globe and its counterpoise were hung from hooks soldered to the bottoms of the pans by means of wires which swung freely through small holes made for the purpose through the bottom of the balance case, and also through the top of the shelf on which the case stood. The enclosure in which the globe and its counterpoise hung was a box made of tinned iron fastened to the bottom of the shelf, and having doors in front like an oven, through which the globe could be removed or hung in position. This case was coated with lampblack on the inside, in order to secure uniformity of temperature; and the air was kept dry by means of two large dishes of sulphuric acid, placed on shelves at the top of the case. We first placed the sulphuric acid dishes on the bottom of the case in the usual way, but we found it impossible thus to secure a uniform condition of the atmosphere within; and as moist air is necessarily lighter than an equal volume of dry air at the same temperature and pressure, it is obvious that any drying material will have the greatest efficiency when placed near the top of the space to be protected. The tin box was itself enclosed in a cupboard, but not otherwise protected; and the balance case was surrounded by curtains, in order to shield the beam from radiation.

With the apparatus so arranged, it was found possible to obtain most satisfactory and concordant results to tenths of a milligram when the change in the temperature of the balance-room was not very rapid; but any sudden changes produced by artificial heating would cause slight currents of air in the interior of the case, whose effect became very sensible, but whose influence we were able to eliminate. The best series of results, however (the second series in the table below), was obtained during the month of June, when there was no artificial heat in the building, and the temperature varied but little during day and night.

The globe used for holding the hydrogen—shown in Fig. 1 in about one sixth of its actual dimensions—has an interior capacity of 4961.5 cubic centimetres, and weighs 570.5 grams. The cap with



FIG. 1.

the connecting tubes was ground into the neck, and this joint, as also the stopcocks, was so carefully made that there was absolutely no leakage, and the globe would hold a vacuum indefinitely; as was shown frequently by its remaining hung on the balance for weeks together when exhausted without change of weight. The apparatus was made by Emil Greiner, of 79 Nassau Street, New York, whose careful workmanship greatly contributed to the success of our investigation. The details of the stopcock are shown at the sides; and it will be noticed that, besides the direct way, there is a side way through the plug of the stopcock independent of the first, by which, when the stopcock is closed, a con-

nection is established with the base of the cock, through which the gas may escape.

Assume now that the interior of the globe has been exhausted, and a gas current established through this side aperture from one of the generators employed. On turning the stopcock, the side aperture is first closed, and then the direct way slightly opened, so that all the gas evolved now passes into the globe; and it was found possible to regulate the current with such nicety as not to cause any sudden changes of tension in the generator, which was always provided with an overflow by means of which the tension could be watched, and according to which the stopcock was regulated.

The filling of the globe was one of the critical points of the determination. It generally occupied from one to two hours, and during all this time it was necessary, with the hand on the stopcock, carefully to watch the tension at the overflow already mentioned, and represented in Fig. 5, and Figs. 7 and 8 of Plate. From the beginning to the end of the operation there was a greater tension in the generator than in the outside air, by about

one inch of mercury. When the connection was once established between the generator and the globe, there was absolutely no leakage through the side way, as was tested in several cases by dipping the mouth of the tube at the base of the cock under mercury.

The whole process of weighing the hydrogen was finally reduced to the following manipulation. The globe was connected by means of a rubber hose with a rotary air-pump having automatic valves, made by E. S. Ritchie, of Boston. It was then exhausted to within 1 mm. of mercury. Next, closing the cock and disconnecting the globe, it was cleaned with distilled water and fine cotton cloth; at least, this was done five or six times during the determinations. But as the globe when out of the balance case was always protected by a cylindrical tin box with a cover, from which the exit tubes projected, it was usually only necessary to clean the exit tubes in this careful manner, simply dusting off the globe with a large camel's-hair brush, before hanging it in the balance case. In this part of the operation it was necessary to take care not to communicate to the globe a charge of electricity by rubbing it with a perfectly dry cloth.

The globe was hung on a wire stirrup, which caught the exit tubes, as the glass joint was sufficiently strong to support the weight of the globe. The globe was so nearly balanced by its equipoise that when exhausted it only required about one decigram to establish equilibrium. The time required to attain perfect equilibrium varied with the conditions. If the glass had been previously cleaned as described above, perfect equilibrium might not be reached for forty-eight hours, or even longer, while, if the glass had only been dusted, twelve hours were generally sufficient.

After the tare had thus been taken, the globe was removed from the balance, placed in the protecting case, and filled with hydrogen as just described. The inlet tube, to which a rubber connector had been attached, was scrupulously cleaned as before, and the globe was again dusted and hung on the balance. During all these transfers the globe was always handled with clean cotton cloth, and the hands never came in contact with the glass. The increased weight was now the weight of the hydrogen; and as the volumes equipoised were exactly the same, and the additional weight was represented by less than five tenths of a gram of platinum, any correction for the buoyancy of the atmosphere is unessential.

Combustion Apparatus.

The apparatus by which the combustion of the hydrogen was made is represented in the Plate accompanying the paper (Fig. 6). It is made up of a series of small combustion furnaces, which are a modification of a kerosene-oil stove called "the American," very much used in the United States. This stove, as adapted to chemical uses by the writer, is shown in Figs. 2 and 3, and it has proved of great value, not only for elementary chemical experiments in school courses, where illuminating gas is not to be had, but also in a well equipped chemical laboratory. The stove is made for burning kerosene oil, but alcohol can also be burnt in it with decided advantage for chemical work. The figure of the stove has been drawn to about one sixth of the actual size.

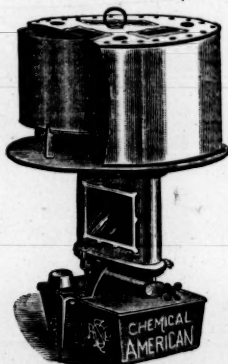


FIG. 2.

In the figure of the combustion apparatus (Fig. 6, Plate) it will be noticed that the globe, protected by its case, stands about in the middle of the line. By means of a suction pump attached to the extreme right of the apparatus, a current of air is maintained through the whole length. Beginning now at the extreme left, the air first passes over reduced copper and is deprived of its

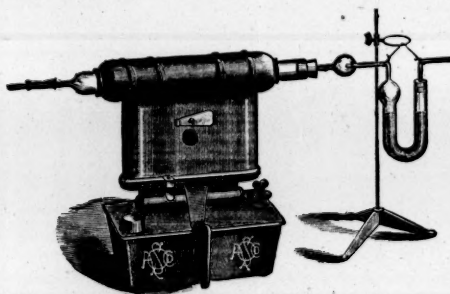


FIG. 3.

oxygen. It next passes over cupric oxide, by which any traces of hydrogen that had remained occluded by the reduced copper, or any traces of hydrocarbons in the air itself, are burnt. It next passes through caustic potash bulbs, and then through a system of driers, meeting successively calcic chloride, sulphuric acid, and phosphoric pentoxide. It now enters the globe through the inlet tube reaching to the bottom, carrying before it the hydrogen into the combustion furnace.

The water from the combustion was collected in a condenser—the details of whose construction are represented in Fig. 4—which was shielded from the furnace by a screen of asbestos paper.

Nine tenths of the water was condensed in the middle tube, and all but the last traces of the aqueous vapor were absorbed by the sulphuric acid through which the air subsequently bubbled up at the bend of the U tube, between glass beads, which broke the ascent and divided the bubbles. With this condenser was connected a U tube containing phosphoric pentoxide, which absorbed the last traces of the aqueous vapor, seldom, however, gaining in weight more than two milligrams during a combustion lasting from seven to eight hours. Then follows a safety tube containing calcic chloride (or in some cases phosphoric pentoxide), to prevent any reflex diffusion, and finally, an adaptation of the principle of Mariotte's flask to regulate the velocity of the air current. It will be seen that the open mouth of the central tube of this last apparatus dips under the mercury in the tall jar, so that by raising or lowering it the strength of the current could be exactly regulated.

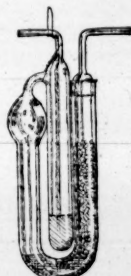


FIG. 4.

Before beginning a combustion, the place of the hydrogen globe was supplied by a straight piece of glass tubing, and the air current maintained through the heated combustion tube until the cupric oxide was perfectly dry. Next the furnace at the extreme left was lighted, and the current continued until the oxygen in the air of the drying tubes had been so far replaced by nitrogen as to remove all risk of subsequent explosion.

Meanwhile the globe and condensing tubes were made ready, and first the globe and next the condensing tubes were placed in position, all the rubber connectors required having been previously

dried in the current of dry air, and the joints were so contrived that subsequently the stream of gas came in contact with the smallest possible surface of the rubber connectors. The combustion lasted, as has been already stated, from seven to eight hours, and during this time quite a rapid current of air was drawn through the apparatus.

Our preliminary experiments plainly showed that the rapidity of the current within practicable limits had no appreciable effect on our results, and this is due to the fact that the current entered the globe and left the condensers under precisely the same conditions. More than nine tenths of the water was condensed during the first half hour, the drops falling regularly from the mouth of the inlet tube, and after two hours all traces of cloudiness disappeared from this tube or its connections, showing that the air coming over was perfectly dry. The water thus collected was absolutely clear and limpid.

After the first hour the combustion furnace used for removing oxygen from the air, at the extreme left, was taken away, and by the end of the combustion the reduced copper in the combustion tube proper was again completely oxidised, leaving the globe and all the tubes filled with normal air, as at the beginning of the process. It only remained now to remove the condensers and reweigh them with all necessary precautions. At both weighings the barometer and thermometer were observed, and the small, usually insignificant correction for buoyancy caused by a change in the atmosphere during the interval was carefully estimated.

The question of the time of running the combustion after the production of water had sensibly ceased was one that was carefully considered. The time mentioned above—eight hours—was far outside the necessary limits, and was reached only after a large number of experiments. That a very long continuance of the current after the combustion was practically ended was unnecessary was clearly shown by several circumstances. In the first place, the duration of the combustion beyond the limit we have named made no difference in our results, as was repeatedly shown. Again, in one instance, after detaching the condensation tubes and weighing them, they were again put in place and the combustion continued three hours longer, during which time the tubes gained no appreciable weight. In another instance, when a suspicion arose that possibly some hydrogen might be occluded on the walls

of the globe, the condensation tubes having been dismantled and weighed as before, the globe was also dismantled and heated over the free flame of a Bunsen lamp to as high a temperature as the glass would safely bear, over 300° C., and then, the apparatus having been remounted, the combustion was continued for one hour. Here again the condensation tubes gained only a small fraction of a milligram in weight, an effect which might easily be accidental, and which was wholly without influence on the result.

Apparatus for preparing Hydrogen.

In the preliminary determinations the hydrogen was drawn from a large copper generator charged with zinc and dilute sulphuric acid. The zinc and sulphuric acid were wholly free from arsenic, and of the best quality, but not absolutely pure; and the writer depended upon an elaborate system of washers and driers for purifying and drying the gas. He found the greatest difficulty in removing the last traces of sulphurous oxide, which hydrogen prepared in this way always carries. The presence of this trace cannot be detected by litmus paper, but is immediately indicated by the production of hydric sulphide when the gas is passed over heated platinum sponge; and by interposing a tube containing platinum sponge maintained at a low red heat, followed by a set of potash bulbs, this impurity can be entirely removed. It can also be removed by washing with a strong solution of potassic hydrate alone, if the gas remains long enough in contact with the solution. It was found, however, that a series of potash bulbs was insufficient for this purpose; but two of the long washers represented in the background of Fig. 5 and in Figs. 7 and 8 (Plate), where the gas in small bubbles travels up a tube $5\frac{1}{2}$ feet long, are sufficient to remove the sulphurous oxide from even a quite rapid current of hydrogen gas. A series of preliminary determinations was made with hydrogen gas thus prepared and purified, and it was obvious from an inspection of the results, as well as from the difficulties which were experienced in keeping all the joints of this complicated apparatus tight, that the irregularities arose from the diffusion of the air into the hydrogen at some one or other of these joints. It was therefore next sought to simplify the apparatus, and to depend upon the purity of materials rather than on the completeness of purifying methods for obtaining pure hydrogen. Meanwhile, for reasons stated below, the writer had reduced very

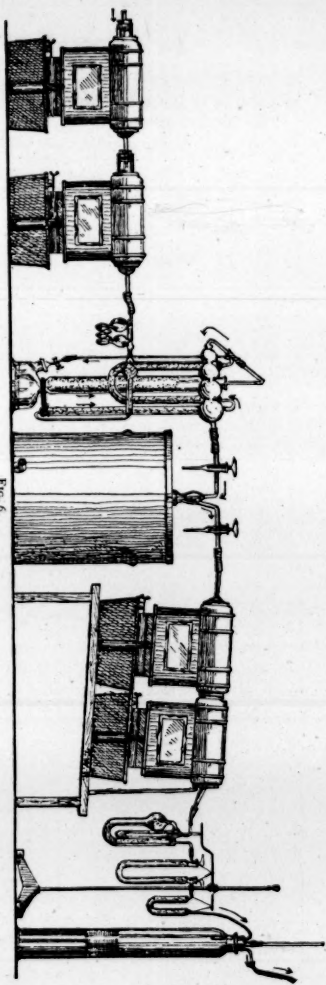


FIG. 6.

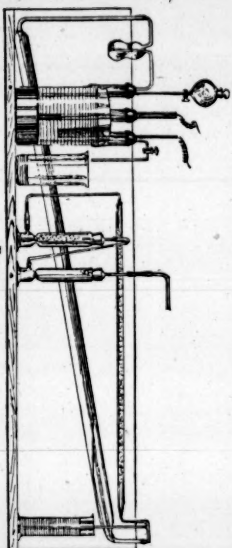


FIG. 7.

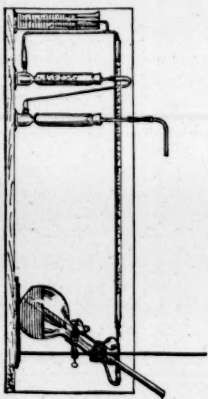


FIG. 8.

materially the scale of his operations, and this rendered unnecessary the large generator we had first employed.

The second apparatus that was constructed is represented in Fig. 5. Of this, the generator, in which hydrogen is made from pure zinc and hydrochloric acid, is the same as that described by Julius Thomsen.¹ The Wolff bottle is filled with pure granulated zinc, and the upper bottle contains pure hydrochloric acid diluted about one half. By means of a glass stopcock the acid is allowed to flow into the zinc drop by drop, and in this way the current of

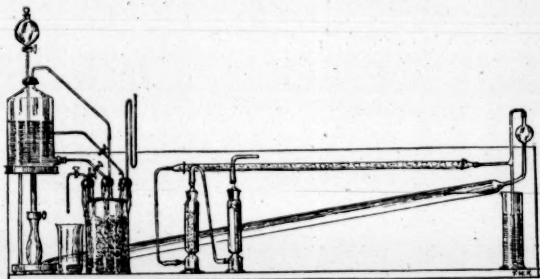


FIG. 5.

hydrogen can be quite closely regulated. Tubes protected by stopcocks are provided for adding fresh charges of acid and for drawing off the solution of zinc chloride; also a tube connecting the upper part of the two bottles enables the operator to effect these transfers without introducing any air. The gas from this generator passed first through a long potash tube inclined at about 10° to the horizon, then through a tube about three feet long filled with calcic chloride, then through a glass tower filled with glass beads drenched with sulphuric acid, and lastly through a second tower filled with phosphoric pentoxide. As many of the joints as possible were made by fusing together the glass, and all the others were protected by a cement consisting of equal parts of pitch and gutta-percha. It will be noticed that an overflow is provided at the point where the potash tube connects with the calcic chloride tube, the open mouth of the overflow tube dipping about six or eight inches deep under concentrated sulphuric acid. This over-

¹ Thermochem. Untersuch. 1, 28.

flow indicated the least change of tension of the hydrogen in the apparatus, and would have shown the least leak if it had existed; but the apparatus as thus constructed remained absolutely tight so long as it was in use.

With the hydrogen drawn from this apparatus, the first determinations were not wholly satisfactory, and the cause of error was traced to the air dissolved in the dilute hydrochloric acid with which the generator was charged. In all the succeeding determinations the greatest pains was taken to remove the last traces of air by boiling the dilute acid and allowing it to cool in a stream of hydrogen; and as additional precaution, while the solution was still warm, the gas was exhausted from the containing vessel and pure hydrogen run in, several times in succession, the pure acid being finally conveyed into the generator entirely out of contact with the air. The need of all these precautions will be seen when it is considered how small an admixture of air or of nitrogen will materially influence the weight of the hydrogen. If only one ten-thousandth of the volume of the hydrogen were replaced by air during the process of filling the globe, this would cause an apparent increase of weight in the hydrogen of five tenths of a milligram, and that, other things being equal, would reduce the atomic weight of oxygen two hundredths of a unit.

The precautions used in filling the globe have already been described in detail, and with hydrogen from the apparatus, constructed and charged as just described, were made the five consecutive determinations whose results are given as of the first series in the table on page 107. These, and all the determinations given in the table, were made by the writer's pupil and assistant, Mr. Theodore William Richards, to whose experimental skill the success of the investigation is largely due, and without whose assistance the work could not have been completed in the present condition of the writer's sight. The mean of these first five results, as will be noticed, is but little less than that obtained by Dumas, and the probable error, ± 0.0048 , is considerably less than that of Dumas. In order to understand how this result appeared to the writer, it must be remembered that he started with a certain prepossession in favor of the hypothesis of Prout, based on his previous work on antimony; and, furthermore, that the effect of the causes of error which had been encountered and overcome all tended to lower the atomic weight; and the result obtained was a maximum which had

been reached after every known precaution had been taken. But although this maximum was essentially the same as that obtained by Dumas by an obviously less direct and less accurate method, yet it was still possible that there might be some constant error, and that some cause might yet be found which would raise the maximum by the forty-six thousandths required to give the whole number 16. It was true that the probable error was only about one tenth of this difference; still, as the materials had been purified, the maximum had constantly risen, and the theoretical limit was in sight. In reviewing the work, it was obvious that the degree of accuracy of the methods used for determining the weights both of the hydrogen and of the water was so great that no possible error in these values could account for the difference in question. This would imply an error of 1.2 milligrams in the weight of the hydrogen, and of 10.8 milligrams in the weight of the water, and the possible error of a single determination—leaving out of account the reduced probable error of the average value—was far within these limits. If there was a constant error, it must result from the want of purity of the hydrogen gas, and we therefore determined to try another method for preparing the hydrogen.

The apparatus next used is represented in Fig. 7 (Plate), and differs from the last only in the generator. Here the generator is a three-necked bottle having a capacity of about two litres, filled to about one eighth of its capacity with a semi-fluid amalgam of mercury and pure zinc. On this rests dilute hydrochloric acid, containing about twenty per cent. of HCl, nearly filling the bottle. Into this acid dips a platinum electrode, while a straight glass tube passing through the middle neck and dipping under the amalgam gives the means of establishing an electrical connection between the large platinum plate which forms the negative electrode and the amalgam. In addition, a siphon tube for drawing off the acid when saturated with zinc, a funnel tube for introducing a fresh charge, and an exit tube, all well cemented to the several necks of the bottle, complete the generator. When the electrical connection is broken, all chemical action ceases, but on connecting by a wire the platinum electrode with the amalgam, a very steady but slow evolution of hydrogen gas takes place, which can be regulated with the greatest nicety by varying the resistance of the connecting wire. On interposing two cells of a Bunsen battery the evolution of gas becomes very rapid. Besides its special use in this connection, the apparatus will be found of great value as

giving an absolutely constant source of pure hydrogen whenever required. In charging the generator with acid the same care was taken to exclude every trace of air as with the previous apparatus, and with hydrogen thus prepared a second series of five consecutive determinations was made, whose results are given in the table on page 107, below those of the first series; and it will be noticed that, while the average value obtained is essentially identical with the previous result, the agreement of the several determinations is more close, and in consequence the probable error is reduced more than one half. A closer agreement under the circumstances could not possibly be expected.

Such a striking confirmation of the previous result seemed very conclusive, and the very small probable error indicated a command of the method which was very satisfactory. Still, it could not be proved that there might not be a constant impurity in the hydrogen used. As the hydrogen had passed every possible chemical test unimpeached, the only possible impurity that could be suspected was nitrogen, and Mr. Richards therefore made a careful spectroscopic examination, searching for the more conspicuous nitrogen lines in the spectrum obtained by passing an induction current through a rarefied atmosphere of the gas from the generator just described; but not the faintest trace of any of these lines could be seen.

Still, as in the electrolytic method of preparing the hydrogen the same materials, hydrochloric acid and zinc, were used as in the first series of experiments, it was determined to procure hydrogen by a wholly different chemical process, using the well known reaction of metallic aluminum upon a solution of potassic hydrate.

The purest aluminum sheet that could be obtained in the American market was procured for the purpose, and the apparatus represented in Fig. 8 (Plate) was used for generating the gas. The generator here was a simple flask holding a strong solution of chemically pure potassic hydrate, and the aluminum was introduced in small pieces through a large open tube—dipping under the surface of the solution—the liquid being maintained at a level near the open mouth of the tube by the tension in the interior of the apparatus. The small strips of aluminum were carefully cleaned, and caused slowly to slide down the tube; the evolution of hydrogen from the surface began as soon as the strips of metal touched the liquid, and became very active in the tube before they dropped into the flask. And this action insured the removal of any traces

of air which might adhere to the surface. In this apparatus the long caustic potash washer was not used, as being no longer necessary, and the gas was passed through caustic potash bulbs to remove the spray, and then through a calcic chloride tube, and over sulphuric acid and phosphoric pentoxide, as before.

With hydrogen thus prepared, the six determinations of the third series in the table were made; and it will be seen that the average of the results is a value which is essentially identical with the average values from the other two series. The probable error in this last series is larger than in the second, although still very small; but the difference is due, as the note-books plainly show, to the different conditions under which the two series were made. As before stated, the compensation of the balance was perfect, and the apparent weight of the globe did not alter by a tenth of a milligram, even with wide variations of temperature and pressure, so soon as those changes became constant. But when the changes of temperature in the balance-room were rapid, currents of air were established in the case, however great care was taken in protecting it, which rendered the apparent weight irregular to the extent of one or two tenths of a milligram; and the third series was made under less favorable conditions in this respect than the second. This point is illustrated by the following notes of two determinations, which are given in full, in order that all the circumstances connected with the determinations may be seen.

SERIES II. *Determination 5.*

Weighings of the globe:

		Grams.
Exhausted.	June 6th, 6.00 P. M. Tare	= 0.1960
	7th, 7.25 A. M.	= 0.2011
	" 8.30 A. M.	= 0.2011
	" 11.20 A. M.	= 0.2011
	" 2.00 P. M.	= 0.2011

0.2011

Filled with Hydrogen.	June 7th, 7.20 P. M. Tare	= 0.6100
	8th, 8.00 A. M.	= 0.6156
	" 10.00 A. M.	= 0.6156
	" 12.15 P. M.	= 0.6154
	" 7.50 A. M.	= 0.6155
	" 9.30 A. M.	= 0.6155
	" 11.40 A. M.	= 0.6155

0.6155

Weight of Hydrogen taken = $0.6155 - 0.2011 = 0.4144$ gram.
The combustion was started at 11 A. M. and stopped at 6 P. M.

Weight of P_2O_5 tube,			
before combustion	= 48.2499	$h = 29.58$	$t = 26.0$
after	= 48.2529	$h = 29.76$	$t = 23.5$
Gain in weight	= 0.0030	+ 0.18	- 2.5

Weight of H_2SO_4 tube,			
before combustion	= 62.3959	$h = 29.58$	$t = 26.5$
after	= 66.1076	$h = 29.75$	$t = 23.5$
Gain in weight	= 3.7117	+ 0.17	- 3.0

The correction to vacuum for 3.7117 grams of water weighed with brass and platinum weights is 4.1 mg.

Gain in weight of H_2SO_4	= 3.7117 grams.
" " P_2O_5	= 0.0030
Correction to vacuum	= 0.0041
" for t and h , P_2O_5	= 0.0004
" " " H_2SO_4	= 0.0005
Total H_2O formed	= 3.7197
Weight H taken	= 0.4144
Weight O combined	= 3.3053

$$\text{Atomic weight of oxygen} = \frac{2 \times 3.3053}{0.4144} = 15.953$$

Per cent. H in water = 11.140. Per cent. O in water = 88.860.

SERIES III. Determination 5.

Weighings of the globe:

Exhausted.		Grams.
	Nov. 8th, 7.45 A. M. Tare	= 0.1127
	" 11.10 A. M.	= 0.1125
	" 12.00 M.	= 0.1122
	" 5.00 P. M.	= 0.1122
	9th, 8.40 A. M.	= 0.1121
	" 9.15 A. M.	= 0.1119
	" 12.40 P. M.	= 0.1120
	" 4.00 P. M.	= 0.1121
	10th, 8.40 A. M.	= 0.1119
	" 10.40 A. M.	= 0.1120
	11th, 8.40 A. M.	= 0.1121
	" 10.15 A. M.	= 0.1120

Average Tare = 0.1120

Filled with Hydrogen.	Nov. 11th, 12.45 P. M.	Tare = 0.5325
"	4.00 P. M.	= 0.5348
"	6.00 P. M.	= 0.5328
	12th, 12.00 M.	= 0.5273
	14th, 8.00 A. M.	= 0.5273
"	9.30 A. M.	= 0.5273
"	11.15 A. M.	= 0.5273
Tare filled with H		= 0.5273
"	empty	= 0.1120
Weight H		= 0.4153

The combustion was started at 11.25 A. M. and stopped at 6 P. M.

Weight of P_2O_5 tube,			
before combustion	= 48.1795	$h = 30.03$	$t = 16.5$
after	" = 48.1832	$h = 30.00$	$t = 18.0$
Gain in weight		= 0.0037	- 0.03 + 1.5

Weight of H_2SO_4 tube,			
before combustion	= 64.9625	$h = 30.03$	$t = 16.5$
after	" = 67.6832	$h = 30.00$	$t = 18.0$
Gain in weight		= 3.7207	- 0.03 + 1.5

Gain in weight of H_2SO_4	=	3.7207	grams.
" " P_2O_5	=	0.0037	
Correction to vacuum	=	0.0041	
		<u>3.7285</u>	

Correction for t and h , H_2SO_4	=	- 0.0002
" " " P_2O_5	=	- 0.0002

Total H_2O formed	=	3.7281
Weight H taken	=	0.4153
Weight O combined	=	<u>3.3128</u>

$$\text{Atomic weight of oxygen} = \frac{2 \times 3.3128}{0.4153} = 15.954$$

$$\text{Per cent. H} = 11.139. \quad \text{Per cent. O} = 88.861.$$

ATOMIC WEIGHT OF OXYGEN.

Table of Final Results.

SERIES I.

Weight of Hydrogen.	Weight of Water.	Atomic Weight of Oxygen.
0.4233	3.8048	15.977
0.4136	3.7094	15.937
0.4213	3.7834	15.960
0.4163	3.7345	15.941
0.4131	3.7085	15.954

$$\text{Average} = 15.954 \pm 0.0048$$

SERIES II.

0.4112	3.6930	15.962
0.4089	3.6709	15.955
0.4261	3.8253	15.955
0.4197	3.7651	15.942
0.4144	3.7197	15.953

$$\text{Average} = 15.953 \pm 0.0022$$

SERIES III.

0.42205	3.7865	15.943
0.4284	3.8436	15.944
0.4205	3.7776	15.967
0.43205	3.8748	15.937
0.4153	3.7281	15.954
0.4167	3.7435	15.967

$$\text{Average} = 15.952 \pm 0.0035$$

$$\text{Total average} = 15.953 \pm 0.0017$$

$$\text{Dumas's value} = 15.960 \pm 0.0070$$

On examining the table it will be noticed that the mean of the determination by the electrolytic method is the mean of all the determinations combined, and that the probable error of the total average is only about one fourth as great as the error of the nineteen determinations of Dumas, which are incomparably the best that have hitherto been made.

It does not now seem possible to escape from the conclusion that the proportions in which the purest hydrogen that can be made combines with oxygen to form water are those of 2 to 15.953, with a possible error far within the $\frac{1}{100}$ of a single unit.

The question, of course, still remains, Is the hydrogen thus prepared the typical hydrogen element? But this is the same question which must arise in regard to any one of the elementary substances; and all that we can say is, that the evidence in regard to the purity of the hydrogen we have used is as good as any that can be adduced in regard to any one of the elementary substances whose atomic weight has been most accurately determined. The question as regards Prout's hypothesis narrows itself now to this one point; and here we must be content to leave it until further investigation has given us more knowledge in regard to the nature of elementary substances.

The writer at first planned to carry out the investigation on a much larger scale, and for the purpose had blown a globe similar to that represented by Fig. 1, but of five times the capacity, and counterpoised it by the same general method. This globe held twenty-five litres (somewhat over two grams of hydrogen gas), or five times as much as the globe actually used; but the difficulties of carrying out the determinations on this scale led him to reduce the scale of the determinations to that actually adopted; and in view of the results finally reached, it is evident that no appreciable advantage would have been gained from the enormous expenditure of time and labor which the process on a large scale involves. Assuming that the difficulties of preparing pure hydrogen gas on that scale could have been overcome, it would have required from five to seven hours to fill the globe, and four or five days continuously to complete the combustion.

Moreover, after many trials, the writer could not procure a globe that would stand the requisite pressure weighing less than two and one half kilograms, and with this weight and volume it was not possible, with the best balance he could command, to distinguish half a milligram with as much accuracy as he could one tenth of a milligram with the smaller apparatus, while a vastly longer time was required to reach equilibrium. A great deal of time was spent in endeavoring to perfect this larger apparatus, and a very thorough knowledge was acquired of its relative efficiency. The greatest gain that could have been expected in carrying out the

work on this scale would have been the reduction of the probable error to about one half of the present amount, but it is obvious that this gain could be of no importance in the present condition of the science. The accuracy we have reached is far beyond the demands of any analytical work; and, as we have shown, the theoretical question in regard to Prout's law has been settled so far as analytical work can solve the problem. It now turns solely on the typical character of the material we call hydrogen, when prepared in the purest condition known to modern science.

In considering the bearing of the result now published on Prout's hypothesis, it must be borne in mind that it confirms in a most striking manner the result of Dumas, based on the weight of oxygen which water contains, and in connection with his results furnishes a complete analysis of water, with a degree of accuracy as great as can be expected, or as has ever been obtained, in any analytical work.

Complete Analysis of Water.

Percentage of oxygen after Dumas, ...	88.864 $\pm$ 0.0044
Percentage of hydrogen according to the present work	11.140 $\pm$ 0.0011
	100.004 $\pm$ 0.0045

It must be remembered that in Dumas's investigation the oxygen alone was weighed, while in the present investigation the hydrogen alone was weighed, and the fact that these two wholly independent analytical results made under such widely different circumstances exactly supplement each other within the limits of probable error, is an evidence of accuracy and a proof of finality which is irresistible.

It would have been highly desirable, if it had been possible, to determine both the oxygen and the hydrogen in one and the same analytical process, as the writer succeeded in doing in the case of silver, bromine, and antimony, and he made many experiments on the reduction of oxide of silver by hydrogen with this view. He succeeded in preparing pure oxide of silver, of definite composition, but the investigation was interrupted by the failure of his sight before he was able to overcome the grave experimental difficulties which the process presented. In view, however, of the present results, it is doubtful whether any advantage would have

been gained by that mode of experimenting, for no more certain confirmation could have been reached than that furnished by a comparison of Dumas's results with those of this paper.

Since this investigation was essentially finished, and the results communicated to the American Academy at their meeting of June 15, 1887, we have received from the author a "Sonderabdruck" from the "Berichte der Deutschen Chemischen Gesellschaft," dated the 26th of July following, and entitled: "E. H. Keiser: Ueber die Verbrennung abgewogener Mengen von Wasserstoff und über das Atomgewicht des Sauerstoffs." In this paper Dr. Keiser distinctly recognises the importance of directly weighing the hydrogen in the determination of the atomic weight of oxygen, and quotes the remarks of Dumas given above. He has also devised a very ingenious method of weighing hydrogen when occluded by palladium; but the preliminary results he publishes are far from having the degree of accuracy required, and lead us to infer that, like our own preliminary results, they must be vitiated by varying impurities in the hydrogen gas used. The three determinations whose results he publishes gave for the atomic weight of oxygen respectively 15.873, 15.897, and 15.826.

We are sorry if Dr. Keiser has entered on somewhat the same field which we have so long occupied without knowledge of our work. But, as above stated, our investigation was begun more than five years ago; and the methods employed have been freely explained to the many chemists, both American and European, who have visited Cambridge during the interval. We earnestly hope that Dr. Keiser will carry out his investigation; for so important a constant as the atomic weight of oxygen cannot be too often verified.

J. P. C. CAMBRIDGE, December 15, 1887.

Contributions from the Chemical Laboratory of Wesleyan University.

VI.—NOTE ON THE ABSORPTION OF AMMONIA BY
ACID SOLUTION IN NITROGEN DETERMI-
NATIONS WITH SODA-LIME.

BY I. S. HAYNES.

Among the possible sources of error in the determination of nitrogen by the method of Varrentrapp and Will is the failure of the ammonia to be completely absorbed by the acid solution, in case the combustion proceeds very rapidly and the ammonia is considerably diluted with other gases. The following determinations were made to test the effect of rapid combustion on the absorption of ammonia, and, incidentally, the danger of small particles of soda-lime being swept past the asbestos plug into the acid solution. Although undertaken simply as one of the series of exercises in the undergraduate course of study and practice in this laboratory, the results may not be unworthy of record.

The method followed was that described in a previous article of this series¹ as usual in this laboratory, except that the packing of the asbestos plug in the anterior end of the tube and the time of combustion were varied, as shown in the tabular statement herewith. The ammonia was caught in an ordinary Knop and Arendt bulb apparatus (with four bulbs) containing 10 cc. of a rather concentrated standard solution of sulphuric acid, of which 1 cc. corresponded to about 10 mgm. of nitrogen. About 0.25 gram of ammonium sulphate mixed with stearin previously proved to be free from nitrogen, was used for each determination, and furnished ammonia sufficient to neutralise about one half of the acid.

In the determinations numbered 1, 2, and 3 in the table, the anterior asbestos plug was some 2-3 cm. long and packed reasonably tight, as is usually done in our work. In No. 4 it was shorter than usual, and care was taken to pack it very tightly by holding the tube perpendicular with the anterior end down and pressing upward against the asbestos with the flat end of a lead pencil. The soda-lime above furnishes a firm backing, so that the asbestos may be packed as closely as desired. Reversing the tube and tapping it gently, its contents will settle down from the asbestos,

¹ This Journal 9, 319.

leaving a space which can be closed up as much as necessary by pushing the compacted plug toward the soda-lime. In Nos. 5 to 7 the plug was put in loosely, as might be done by a careless operator. The figures in the table for number of bubbles per minute were estimated by countings of the numbers in different minutes, and are of course only approximate. In Nos. 4 and 7 the effort was made to push the combustion as rapidly as could be done without danger of accident. The flow of gas was much more rapid and the bubbles were much larger than would be the case in any ordinary well conducted analysis. This will readily be seen when we consider that the quantity of diluting gases, from the decomposition of nearly a third of a gram of stearin in each case, was large, and that the time of the combustion was only 12 minutes, instead of from 30 to 60 minutes which the combustion commonly takes. Add that the quantity of acid solution was rather small, only 10 cc., and it is evident that the conditions were very unfavorable for complete absorption of the ammonia. The percentages of nitrogen in Nos. 1 to 4 average 21.14. This figure accords very closely with those obtained by other gentlemen who made determinations of nitrogen in the same material and at the same time by the soda-lime and other methods.

Determinations of Nitrogen in Ammonium Sulphate.

Number.	Asbestos Plug.	Rapidity of Combustion.	Time of Combustion, Minutes.	Number of bubbles per minute. Approximate.	Ammonium Sulphate used, Grams.	Nitrogen found, Per cent.
1	Moderately tight.	Rather slowly.	60	60	0.2457	21.12
2	" "	Moderately fast.	35	70	0.2458	21.15
3	" "	" "	35	70	0.2458	21.15
4	Short and very tight.	Very " "	12	90	0.1796	21.16
5	Loose.	Rather " "	25	70	0.2630	21.49
6	Short and loose.	Very " "	13	85	0.2558	21.69
7	Long " "	" "	12	90	0.2928	21.37

Comparison of the figures in the last column of the table shows no loss of nitrogen, even in No. 4, in which the flow of gas was so rapid and the bubbles were so large. To still further test whether ammonia escaped absorption, a second bulb tube with acid solution

was connected with the first so that the gases which came from the first passed through the acid in the second. Even in No. 4, Nessler's test gave no reaction for ammonia in the second tube. It is clear, then, that despite the considerable dilution and extremely rapid flow of the gases through the 10 cc. of acid solution, no ammonia escaped absorption. But it is to be remembered that the quantity of ammonia was only equivalent to about half of the acid in the solution.¹

The large figures of "nitrogen found" in Nos. 5, 6, and 7 are evidently due to the fine particles of soda-lime which were carried through the loosely packed asbestos plugs by the rapidly passing gases. The necessity of proper packing of the asbestos plug is too obvious to need dwelling upon.

The principal fact brought out in these experiments is that the ammonia, the quantity of which was considerable, was completely absorbed by the acid solution in the cases where the combustion was completed in as short a time as twelve minutes, and where the flow of gas was far more rapid than would occur in any ordinary work. The inference is that the absorption of the ammonia is more certain, and the danger of loss less, than is frequently supposed.

VII.—ON CERTAIN SOURCES OF LOSS IN THE DETERMINATION OF NITROGEN BY SODA-LIME.

By W. O. ATWATER AND E. M. BALL.

The object of the following experiments was to test the effect of open space between the soda-lime and the upper wall of the tube (channel, as often recommended), and of lengthened time of sojourn of gases in the combustion tube, upon the amount of nitrogen obtained in the form of ammonia in the determination by the soda-lime method. The determinations were conducted by the method described in the previous article of this series² as usual in this laboratory, except that:

1st. In some cases the tube was packed so full with soda-lime as to leave no considerable channel, in accordance with our usual practice, while in others less soda-lime was used, enough to fill perhaps from four fifths to two thirds of the whole interior of the tube. The channel left was thus quite large.

¹ See Gassend and Quantin, *Zuschr. anal. Chem.*, 1882, 278.

² This Journal 9, 319.

2d. The anterior layer consisted in some cases of finely powdered soda-lime like that with which the nitrogenous substance is mixed for combustion, instead of the coarse particles with which (to secure more contact between the passing gases and the soda-lime and hence more complete ammonification) we commonly fill the anterior part of the tube.

3d. In some cases the combustion tube and the anterior layer of soda-lime were made longer than usual.

4th. The combustion in some cases occupied the usual time, about three quarters of an hour; in others it was prolonged to two and a half hours, as is done by some chemists.¹

It seemed desirable that the trials be made with a substance which had been found by other observers frequently to fail to yield all its nitrogen in the form of ammonia. For this casein was selected.²

To test the accuracy of the nitrogen determinations when made by soda-lime in the usual way, comparative tests were made with Kjeldahl's method in two specimens. In the determinations with soda-lime, the precautions as to compact filling of tube, heating of anterior layer before applying heat to mixture of soda-lime and nitrogenous material, moderate heating throughout and moderate time of combustion, previously mentioned as usual in this laboratory, were observed. The results of these comparative tests are stated in Table I.

TABLE I.

Nitrogen obtained from Casein by Soda-lime and Kjeldahl Methods.

Casein.	Nitrogen found, per cent.			
	Soda-lime Method.		Kjeldahl Method.	
	Separate Determinations.	Average.	Separate Determinations.	Average.
First specimen.	12.20	12.11	12.07	12.07
	12.10			
	12.10			
Second specimen.	12.05	12.44	12.07	12.43
	12.44		12.44	
			12.41	
	12.43	12.44	12.43	12.43

¹ E. g. Nowack, Sitzb. Akad. Wien, **64** Bd., 1871, p. 153; Seegen and Nowack, Pf. Arch. **7**, 1873, 290; Musso, Ztschr. anal. Chem. **16**, 1877, 414.

² The analyses were performed by Mr. Ball in the course of practice for students in this laboratory.—W. O. A.

The determinations in the "first specimen" were preliminary, and the duplicates with soda-lime are somewhat wide apart. The "second specimen" was used for the determinations of Table II, in which those of series A are the same as given in Table I.

TABLE II.

Nitrogen Determinations in Casein by Soda-lime under Different Conditions.

Series.	Length of Tube.	Anterior layer of Soda-lime.		Packing of Tube.	Time of combustion, approximate.	Color of acid after combustion.	Nitrogen found.
		Length.	Kind.				
A	cm.	cm.					prct.
	38	12	Coarse.	No channel.	45 minutes.	Nearly colorless.	12.44
	38	12	"	"	"	"	12.43
B	38	12	Fine.	Channel.	"	"	12.25
	38	12	"	"	"	Slightly colored.	11.85
	38	12	"	"	"	Very dark.	11.66
C	38	7.5	"	"	"	Amber colored.	12.38
	38	7.5	"	"	"	Colorless.	12.00
	38	7.5	"	"	"	Very dark.	10.51
D	38	12	Coarse.	No channel.	2½ hours.	Slightly colored.	12.27
	38	12	"	"	"	"	12.05
	38	12	"	"	"	"	12.05
	38	12	"	"	"	"	11.96
E	38	12	Fine.	Channel.	"	"	12.44
	38	12	"	"	"	"	12.25
	38	12	"	"	"	"	12.20
	38	12	"	"	"	"	12.15
	38	12	"	"	"	"	11.96
F	38	12	"	"	"	"	9.48
	38	12	"	"	"	"	3.92
G	43	17	"	"	"	"	3.14
	48	22	"	"	"	"	2.55

* At very high heat.

The percentages of nitrogen, calculated on water-free casein, as before, are stated in detail in Table II, and are concisely recapitulated in Table III.

TABLE III.

Recapitulation of Results of Nitrogen Determinations by Soda-lime under Different Conditions.

Series.	Soda-lime.			Time of combustion.	Nitrogen found.			Average loss of Nitrogen in per cent. of total Nitrogen.
	Anterior layer.		Packing.		Maximum.	Minimum.	Average.	
	Kind.	Length.						
		cm.			per ct.	per ct.	per ct.	per cent.
A	Coarse.	12	No channel.	$\frac{3}{4}$ hour.	12.44	12.43	12.43	...
B	Fine.	12	Channel.	"	12.25	11.66	11.92	3.3
C	"	$7\frac{1}{2}$	"	"	12.38	10.51	11.63	6.4
D	Coarse.	12	No channel.	$2\frac{1}{2}$ hours.	12.27	11.96	12.08	2.8
E	Fine.	12	Channel.	"	12.44	9.48	11.75	5.5
F	"	12	"	" †	one	det'n.	3.92	68.5
G	"	*	"	"	3.14	2.55	2.85	77.0

* 17 and 22 cm.

† At very high heat.

It thus appears that in the experiments of Tables I and II:

When the determinations were made with the precautions named, series A, the duplicate results agreed as closely with each other and with those by the Kjeldahl method as could be desired. This, taken in connection with the facts reported in other papers of this series, constitutes strong evidence of the correctness of the figures for percentages of nitrogen.

In series B a channel was left over the soda-lime in the tube, the other conditions were the same as in A. The percentages of nitrogen fell to an average of 11.92. Taking 12.43, the average of the results obtained in the series A and by the Kjeldahl method, as actual per cent. of nitrogen, this makes a loss of 0.4 per cent. of the weight of the water-free casein, or 3.4 per cent. of the total nitrogen.

Series C was a duplicate of B, except that the anterior layer consisted of fine particles of soda-lime, thus offering slightly less surface for contact of volatile nitrogenous products with the latter. The percentages of nitrogen were slightly less than in B. The average was 0.8 short of 12.43 per cent., which makes a loss of 6.4 per cent. of the total nitrogen. That the loss in this series averaged so much more than in the previous one may be largely accidental. The loss in the individual determinations ranges from 0.4 to 15.4 per cent. of the total nitrogen. Both the small amounts of nitrogen obtained and the wide variations in the results bear

witness to the error introduced by leaving the channel in the tube. It seems to us most probable that this loss is mainly due to incomplete ammonification of nitrogenous decomposition products. In series A, in which the tube was closely packed with soda-lime, these latter were brought more into contact with the heated soda-lime, i. e. with heated water-vapor, and their nitrogen was completely changed to ammonia. In series B and C, in which there was considerable open space in the tube, the contact with soda-lime would be less intimate, and the ammonification might on that account be less complete. At the same time it is possible that the slower current of gas, consequent upon the larger open space, might, by exposing the ammonia for a longer time to the heat, lead to dissociation.

In series D the determinations were made by the usual method, except that the time of combustion was two and a half hours instead of three quarters of an hour. The loss of nitrogen varied from 1.3 to 3.8 per cent., and averaged 2.8 per cent. of the total nitrogen. An article to follow this will give reasons for attributing the larger part of this loss to dissociation of ammonia during its long sojourn in the tube, though it may be partly due to incomplete ammonification. Briefly stated, they are that (1) the longer exposure to heat, which is longer in proportion than the difference in time would imply, would favor dissociation, and (2) there may have been lack of moisture from the anterior layer of soda-lime after the latter had been heated some time, and this lack may have been unfavorable to complete ammonification but favorable to dissociation.

In series E the conditions were the same as in D, except that a channel was left above the soda-lime. The variations in results and the losses of nitrogen were still greater, the latter ranging from 0.0 to 23.7, average 5.5 per cent. of the total nitrogen. For the case in which all or nearly all the nitrogen was obtained we have no satisfactory explanation, and can only state the results as obtained. That the average loss should be greater and the range of variation wider with a channel than without it is easily accounted for, on the ground that the current of outflowing gases would be slower and the ammonia hence exposed for a longer time to the heat by which it is dissociated.

The single determination F differed from those of E in that the heat was as high as the tubes would endure without bursting. The two in series G differed from those of E in the greater length of

the anterior layer of soda-lime. The nitrogen lost in F and G ranged from 68.5 to 79.5 per cent., or from two thirds to three fourths of the whole. That the lowest results of all should have been obtained with the high heat and very long tubes is easily explained by assuming that the loss of ammonia by dissociation increased with increase of heat and with increase of time of exposure to heat.

To test the working of the soda-lime method with a substance in which the complete ammonification of the nitrogen is more difficult, a series of trials were made with strychnine. The determinations were made by what has been spoken of as our "usual method," except that—

1st. In several cases extra large combustion tubes were employed to allow a larger proportion of soda-lime for mixing with the substance.

2d. In two cases (Nos. 3 and 4 of Table IV) especial pains were taken to put the mixture of fine soda-lime and substance (about 1 part of substance to 40 of soda-lime) along the lower side of the large tube, and to cover it with fine soda-lime, so as to insure passage of the decomposition products through the covering layer of soda-lime, and thus secure more perfect contact of distillation products with soda-lime. The mixture was got into place by aid of a thin narrow tube inserted into the wide combustion tube.

How ineffectual the attempts were to secure complete ammonification of the nitrogen is shown by the figures of Table IV, in which the figures for "Nitrogen found" are those obtained by titration with standard alkali in the usual way. The acid in the bulb tube after combustion was turbid in every case.

TABLE IV.

Percentages of Nitrogen obtained from Strychnine by Soda-lime.

No.	Substance Used. Gram.	Internal Diameter of Tube, Cm.	Nitrogen Found. Per Cent.
1	.5	1.25	6.47
2	.5	1.25	7.64
3	.2	2.	5.88
4	.2	2.	7.35
5	.1	2.	1.57
6	.1	2.	1.70
7	.1	2.	5.88
8	.1	2.	3.92
9	.05	1.25	1.96

In brief, the greatest care in pulverising the substance finely, mixing intimately with soda-lime, using excessive quantities of soda-lime, and packing the tube closely to avoid channel, were ineffective. Insuring the greatest contact of substance and distillation products with soda-lime and most careful heating evidently do not prevent escape of nitrogen in other forms than ammonia. Attempts to get all the nitrogen as ammonia by Kjeldahl's method were also unsuccessful.

The main outcome of the experiments above detailed may be summarised in few words.

1. In combustions with soda-lime, an open space (channel) in the tube is unnecessary and involves danger of loss of nitrogen. This loss may be due to nitrogenous distillation products which escape ammonification, or to dissociation of ammonia, or to both.

2. Prolonging the time of combustion unduly may induce loss. The most probable cause of this loss would seem to be dissociation of ammonia.

3. High heat increases danger of loss, probably by dissociation of ammonia, especially when open space in the tube or slowness of combustion, or both, leave the gases for a considerable time exposed to the action of the heat and not in intimate contact with the soda-lime.

4. With casein (and the data cited and to be cited in the other articles of this series imply that the same is true for the protein compounds of animal and vegetable tissues generally) sufficient contact between soda-lime and substance at moderately high heat suffices to convert all the nitrogen into ammonia. This is effected by intimate mixture of soda-lime and substance, providing a moderately long anterior layer of soda-lime, close packing of the tube, heating the anterior layer well before the heat is applied to the mixture, and keeping it well heated until the operation is done.

5. There are, however, substances, such as strychnine, which, when heated with soda-lime, yield distillation products that are very difficult of ammonification.

A succeeding article will refer to these points in more detail, discuss loss by incomplete ammonification and dissociation, and refer to a probable explanation which they give of the failure of the soda-lime method to bring satisfactory results in some of the cases most frequently cited in evidence of its unreliability.

THE CHEMICAL STRUCTURE OF THE NATURAL SILICATES.

By F. W. CLARKE.

In any attempt to discuss the chemical structure of the inorganic silicates we are met at the outset by difficulties which are partly real and in part imaginary. On the one hand we have to deal entirely with non-volatile solids, of which, because of their fixedness, we cannot certainly ascertain the true molecular weights. They are, furthermore, insoluble and, chemically speaking, non-plastic; that is, they yield but stubbornly to reagents, so that the changes of which they are structurally capable can rarely be studied in the laboratory. These difficulties are very real. On the other hand, most of the definite silicates are natural minerals, and as such are commonly supposed to have a bewildering complexity of constitution. This difficulty is only apparent, not real, and is due to several causes. First, few mineral species occur in a state of even approximate chemical purity; and secondly, many of them, being isomorphous, crystallise together to form seemingly homogeneous bodies to which rational formulae can hardly be assigned. Impurities, indefinite crystalline mixtures, and defective analyses account for many apparent complications. Eliminate from any group of natural silicates these disturbing conditions, and we shall find in every case a simplicity of composition far removed from the complexity which is popularly assumed. Even on theoretical grounds we should expect simplicity of structure. The mineral silicates are, as a rule, exceedingly stable compounds, while complex molecules are relatively unstable. They are formed in nature under conditions of high temperature, or are deposited from solutions in which many reactions are simultaneously possible; circumstances that are strongly adverse to any great complications of structure. Finally, they are quite limited in number, only a few hundred at most being known; whereas, if complexity was the rule among them, slight variations in origin would produce great variations in character and millions of different minerals would be generated. That few substitutions occur is presumptive evidence that only few are possible, and hence simplicity of con-

stitution is to be inferred. In fact we find the same small range of mineral species occurring under the same associations in thousands of widely separated localities, a few typical forms containing a few of the commonest metals being almost universally distributed. The longer the evidence is considered, the more overwhelming the argument for simple silicate structures becomes.

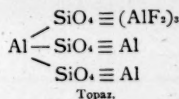
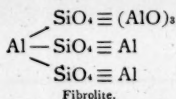
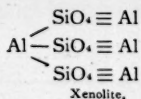
Suppose now that for any given silicate the empirical composition has been ascertained, how can its chemical structure be determined? We cannot measure its vapor density and so deduce its molecular weight; but the problem is not therefore necessarily hopeless. Several lines of available evidence are open. In some cases the compound may be synthetically reproduced in the laboratory, a kind of mineralogical investigation in which rapid progress is now being made. Again, the constant association of the species with certain others sheds light upon its genesis, and still oftener its alterations in nature furnish important details. An alteration product, despised by the crystallographer, is really a record of chemical change, and such products may be of the highest scientific interest. In a few researches they have been produced artificially by reactions which were prolonged for months at a time, and so a mass of evidence is slowly accumulating, strictly analogous in kind to that which the organic chemist chiefly depends upon for ascertaining the structure of a hydrocarbon. All these lines of evidence are legitimate, and all converge towards truly scientific conclusions. We know that certain silicates originated together, and that each alters in certain definite ways; and from these facts we may draw perfectly fair inferences as to chemical structure, and deduce rational formulae which shall give fuller expression to our knowledge. The evidence for such formulae is less perfect than that at the command of the carbon chemist, but it is none the less substantial so far as it goes. It is, furthermore, cumulative.

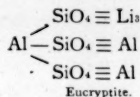
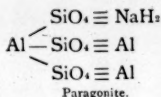
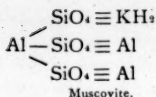
About three years ago, while I was working tentatively at the problem now under discussion, I received for examination certain specimens of topaz which were deeply altered upon their surfaces. Upon investigation the alteration product proved to be a variety of muscovite, and a study of the empirical formulae of the two minerals revealed an unexpected relation between them. Further study brought out more extended relations connecting them with several other silicates, and by a natural series of steps I was led to adopt as a working hypothesis the supposition that double salts

might be regarded as substitution derivatives of normal salts. This hypothesis, since then steadily applied to the discussion of the silicates, appears to be supported by a weighty mass of evidence, and it leads to the development of a series of structural formulae which satisfy many conditions. They express and interpret known relations, lead to the detection of others, and point out suggestive and profitable lines of research. By these tests any hypothesis must stand or fall, and one which, meeting them successfully, has at the same time philosophical significance, may be fairly looked upon as valid.

That the great majority of the natural silicates are double salts need hardly be stated, and that a very great number of them contain aluminum is also a commonplace of chemistry. Of the latter some are orthosilicates, and some are meta-compounds; and the problem is to show how each series may be derived from its corresponding normal salt. As the orthosilicates are the most important, we may begin with their consideration. They represent the maximum of complication and offer the greatest difficulties.

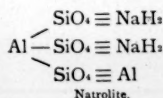
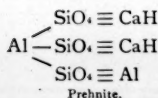
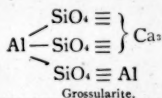
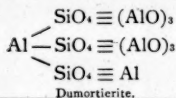
Fortunately, the orthosilicate of aluminum, $\text{Al}_2(\text{SiO}_4)_3$, occurs in nature as the mineral xenolite. This species, which is now well established, was long thought to be an impure variety of fibrolite, Al_2SiO_5 ; and in their optical properties the two are apparently identical. Fibrolite bears the closest of relations to its isomer, andalusite; and to the latter, topaz, $\text{Al}_2\text{SiO}_5\text{F}_2$, is crystallographically akin. Topaz, as I have already stated, alters into muscovite, $\text{Al}_2\text{KH}_2(\text{SiO}_4)_3$; and so also does eucryptite, AlLiSiO_4 . To these compounds we may add paragonite, which is merely a sodium mica, and we have at least six silicates, including the normal salt, which are all evidently related to each other. That their empirical formulae show little or no connection is due to the fact that they do not represent true molecular weights, and on this point our fundamental hypothesis gives us a key to the problem. If we triple the formulae given for fibrolite, topaz, and eucryptite, the substitution theory which I have suggested at once becomes applicable, and the derivation of all the others from xenolite is easy. The following structures will make this conception clear:





In the second of these formulae the univalent group — Al = O is assumed, and in the third we have the corresponding group — Al = F₂. I think no chemist will regard these assumptions as strained.

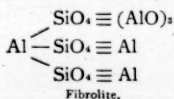
Now the foregoing symbols all represent a series of salts derived from the first one by various substitutions of a single aluminum atom. But further replacements are theoretically possible, and the following minerals seem to illustrate them :



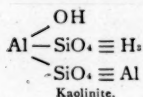
Dumortierite, which has been little studied, appears to be related to fibrolite, and the formulae exhibit a relation. Grossularite, the lime alumina garnet, is a common associate of muscovite, a fact which lends verisimilitude to the formula given above. The other two formulae represent the known composition of prehnite and natrolite, but whether they indicate any deeper relations is not yet proven. They do, however, suggest lines of investigation, and so far fulfill a useful purpose. If they are true, prehnite should be derivable from garnet, and garnet and muscovite ought to be mutually derivable from each other. That garnets do alter into micas is already well known, although the exact character of the change is undetermined, and the micas involved in the reaction appear to be more complex than muscovite.

Returning now to fibrolite, we find that it is a mineral which is liable to alter through a process of hydration. Some of its alteration products have been described as species, notably under the names wörthite and westanite, the latter being apparently the final

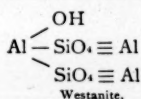
product. Certain other species of the same group frequently undergo a sort of degradation into clays, which, unfortunately, are often too impure to admit of precise formulation. Still, of the several clays which are certainly definite, two seem to fall into series with fibrolite and westanite, as the following structures show:



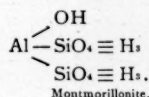
Fibrolite.



Kaolinite.

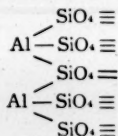


Westanite.

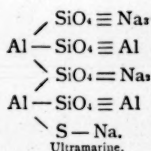
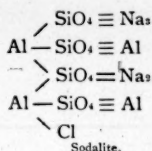
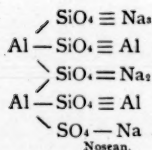
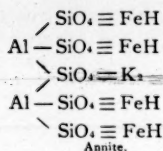


Montmorillonite.

Now, suggestive as these formulae are, they represent only a selection out of a much larger number, all of which seem to follow essentially the same structural rule. If the case rested here it would still be a strong one, but it becomes even stronger when we study some of the more complex orthosilicates, and some of the silicates containing other inorganic acids. In most of the foregoing instances we have one aluminum atom linked with three of the orthosilicic groups, and making a sort of fundamental nucleus to which the other atoms of each molecule are attached. But in many cases we seem to have a semi-polymerisation of that nucleus which results in the elimination of one of the silicas, leaving a new group of atoms which may be represented as follows:

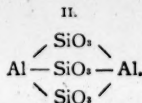
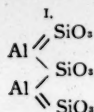


This group, saturated by various bases, seems to exist in many natural silicates, notably among the iron and magnesian micas; and from it certain mixed salts, like sodalite and nosean, may be represented as derived. Thus, to cite a few examples, we may write:



The last of these four formulae is purely hypothetical and rests upon the recognised mineralogical analogies between lapis lazuli and nosean. It is, however, a formula which should be capable of synthetic verification, for ultramarine, itself a product of synthesis, yields many derivatives, the formation of which can be systematically studied. Possibly the lines of research followed by Lemberg, in his work on the alterations of elacolite, may be fitly applied to the investigation of lapis lazuli. As for annite, I have discussed its relations, together with those of the lithia micas, in a previous paper,¹ in which I have also given some suggestions concerning the part played by fluorine in lepidolite, cryophyllite, and phlogopite. Sodalite and nosean were considered in a still earlier paper,² in connection with cancrinite, nephelite, and other species. It is hardly necessary to repeat either discussion here.

Passing now to the metasilicates, we find ourselves, as regards the aluminous salts, at some disadvantage. The normal compound, $\text{Al}_2(\text{SiO}_3)_3$, is not known to exist by itself in nature, although certain of its derivatives are common. Its formula, however, may be written in two ways, as follows, and to one of these types some of the double aluminous metasilicates should conform :

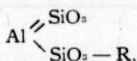


¹Amer. Journ. Sci., Nov. 1886.

²Amer. Journ. Sci., April, 1886.

Which of the two is best sustained by evidence?

To answer this question we may appeal to several well known minerals, such as spodumene, $\text{AlLi}(\text{SiO}_3)_2$, jadeite, $\text{AlNa}(\text{SiO}_3)_2$, leucite, $\text{AlK}(\text{SiO}_3)_3$, and pyrophyllite, $\text{AlH}(\text{SiO}_3)_2$. All of these can be generalised under one formula, thus:



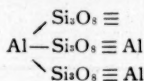
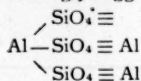
which is directly derivable from normal salt No. 1, and is not derivable from No. 2. Furthermore, kyanite, an isomer of fibrolite, Al_2SiO_5 , is regarded by Groth and others as a basic metasilicate, for reasons which need not be reconsidered here. As such its formula is $\text{Al}_2(\text{SiO}_3)_2\text{O}_2$, which may be derived from either of the formulae for the normal compound. But pyrophyllite often occurs as the gangue of kyanite, which suggests a genetic relation between the two, and so makes it highly probable that the latter mineral should be written



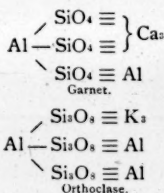
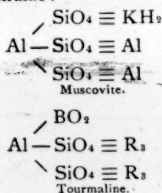
rather than as a derivative of the second formula for $\text{Al}_2(\text{SiO}_3)_2$. Formula No. 1, then, is the more probable formula for aluminum metasilicate. Two isomers may be possible, but the evidence so far favors only one compound.

In addition to orthosilicic and metasilicic acids, at least two other silicic acids correspond to known salts. These are the compounds $\text{H}_2\text{Si}_2\text{O}_5$ and $\text{H}_4\text{Si}_3\text{O}_8$. Still more are possible, but it is not necessary to assume them in order to account for known minerals. Derived from $\text{H}_2\text{Si}_2\text{O}_5$ we have a few species, notably petalite, $\text{AlLi}(\text{Si}_2\text{O}_5)_2$, which is the equivalent of spodumene in structure. The other acid, $\text{H}_4\text{Si}_3\text{O}_8$, is represented only by the species albite and orthoclase, $\text{AlNaSi}_3\text{O}_8$ and AlKSi_3O_8 respectively. If we triple these formulae we have structures quite analogous to the orthosilicates, in which the normal aluminum salt $\text{Al}_4(\text{Si}_3\text{O}_8)_3$ is the starting point for derivation. Now it is universally believed, in accordance with the views of Sterry Hunt and Tschermak, that the triclinic feldspars consist of various mixtures between albite and anorthite as two extremes. If our fundamental hypothesis is true, each of these minerals is derived

by substitution from a normal salt, and the formulae so deduced become strikingly suggestive :



Anorthite is the lime salt corresponding to the first formula, and albite is the soda salt corresponding to the second. Another comparison is even more striking. The four silicates most frequently associated with each other in granite veins are muscovite, garnet, albite or orthoclase, and tourmaline. Tourmaline, according to the analyses made by Mr. Riggs in the laboratory of the United States Geological Survey, is always represented by the general formula $\text{R}'_2\text{BO}_3(\text{SiO}_4)_3$, in which at least the equivalent of R'_2 is present as aluminum. This gives us the following quartette of formulae :



The suggestiveness of these symbols can hardly be questioned. All four are covered by the one general hypothesis; and tourmaline, furthermore, is known to alter into muscovite.

Leaving the aluminous salts, the other silicates present few structural difficulties. Isomorphous mixtures become perhaps more common, but when they are resolved into their constituents relatively simple compounds are found. The commoner bivalent metals form both ortho- and metasilicates, and to them the substitution hypothesis, as a rule, easily applies. Only in the metasilicate series do we find notable difficulties, and they may be avoided by the assumption of polymeric molecules. Thus, instead of $\text{R}''\text{SiO}_3$ we should write $\text{R}''_2(\text{SiO}_3)_2$, in which one atom of R'' becomes replaceable. This conception is by no means new, and is indeed quite commonly in use; but I may be permitted to cite one item of evidence in its favor. When solutions of calcium chloride and sodium metasilicate are mixed, a white precipitate

of calcium metasilicate is thrown down. This reaction I have studied under various conditions of temperature and concentration, and I find that when the precipitated salt is carefully dried over sulphuric acid it has the composition $2\text{CaSiO}_3 \cdot 5\text{H}_2\text{O}$. That is, the double molecule $\text{Ca}_2\text{Si}_2\text{O}_6$ is required in order to avoid a formula containing a half molecule of water. By itself this fact is not of weighty importance, but it counts for something in confirmation of the prevalent views.

Concerning mixed silicate molecules, partly ortho- and partly meta-compounds, I have nothing at present to say. Such silicates undoubtedly exist, as well as aluminous silicates derived from normal salts of magnesia or lime. Nor do I venture to assert that all known silicates are as yet interpretable by simple structural means. There are many outstanding cases which still seem very obscure, but which I confidently expect will be cleared up in time. The micas, chlorites, and scapolites especially need a great deal of farther study. Various theories have been proposed to account for the composition of these groups, but not one is absolutely conclusive and satisfactory. The new method of discussion which I have proposed is yet to be fully applied to these minerals, but a wider knowledge of their variations is essential to its complete application. Whether the method shall be finally established as valid remains to be seen, but its results so far at least entitle it to respectful consideration. As a working hypothesis the substitution theory has value, even though it should be ultimately overthrown.

In conclusion, there is one question to be considered. With the silicates the supposition that double salts are substitution derivatives of normal salts appears to work exceedingly well. But how about double salts in general? With such compounds as the sulphates, chromates, tartrates, oxalates, etc., there seem to be few difficulties; but with the double haloids, acetates, formates, etc., the case is not so clear. Their explanation is troublesome, at least in accordance with current views concerning the valency of their acid radicles; but those views are not absolutely incapable of modification. There may be exceptions to the general hypothesis of derivation, but chemists are not likely to be satisfied with partial theories, and all double salts ought to come under one common law. Toward that ultimate purpose the present paper tends, even though the road which it opens may not reach the final goal.

Contributions from the Chemical Laboratory of the University of Cincinnati.

XXXIV.—ON THE AMINE SALTS OF BENZENE-SULPHONIC ACID.¹

BY T. H. NORTON AND J. H. WESTENHOFF.

Hitherto no amine derivatives have been prepared from the numerous aromatic sulphonic acids, with the exception of the aniline salt of benzene-sulphonic acid obtained by Gericke,² but not analysed.

It seemed desirable to fill to some extent this void in the list of sulphonates, and for that purpose a number of salts were prepared by the combination of various fatty and aromatic amines with benzene-sulphonic acid, the simplest member of its group.

The sulphonic acid used in the following experiments was prepared by the method of Michael and Adair,³ which consists in simply heating together equal parts of benzene and concentrated sulphuric acid with a condenser for about 30 hours. About three quarters of the benzene was changed into acid by this operation. The product was poured into water and neutralised in the ordinary manner by the addition of barium carbonate. By the careful addition of the necessary amount of sulphuric acid to the solution of barium sulphonate, the base was entirely removed, and the filtered solution contained the pure sulphonic acid. This solution of benzene-sulphonic acid, or the crystals obtained from it by concentration, were used in the preparation of the salts to be described.

Benzene-sulphonic acid.—According to Otto⁴ this acid is obtained in the form of very deliquescent needles, which, when dried over sulphuric acid, contain $1\frac{1}{2}$ molecules of water of crystallisation. Hübner⁵ states that it consists of large plates with 1 molecule of water of crystallisation, and gives the melting point as 40° – 42° .

By careful concentration of the aqueous solution of the acid we obtained it in the form of fine needles, exceedingly deliquescent. No traces of crystallisation in plates could be observed. The needles when thoroughly dried between bibulous paper melted at 43° – 44° . On heating the fused acid to 150° , thereby driving off

¹ The material of this and the two following papers was prepared in connection with an extended study of the derivatives of typical aromatic sulphonic acids, now being prosecuted in this laboratory.—T. H. N.

² Ann. Chem. (Liebig) **100**, 217.

³ Ann. Chem. (Liebig) **141**, 369.

⁴ Ber. d. chem. Ges. **10**, 585.

⁵ Ann. Chem. (Liebig) **223**, 240.

the water of crystallisation, the melting point of the anhydrous acid was found to be 50° – 51° . The anhydrous acid solidifies in a fibrous crystalline mass. It decomposes slowly above 155° . The hydrated crystals are insoluble in ether and carbon disulphide, very slightly soluble in benzene, and exceedingly soluble in alcohol and water.

Methylamine benzene-sulphonate, $C_6H_5.SO_3H.NH_2CH_3$.—This salt was obtained by adding a 33 per cent. aqueous solution of methylamine in slight excess to the concentrated solution of benzene-sulphonic acid. On concentration by boiling the excess of the amine was driven off and crystals of the salt were formed. The salt crystallises in fine white needles, joined together in rosettes, and is not easily obtained otherwise than in a fibrous mass, on account of its extreme solubility. The crystals contain no water of crystallisation and are very deliquescent. They melt at 147° . The salt is insoluble in benzene, ether, and carbon disulphide. It is soluble in its own weight of alcohol and of cold water, and in a much smaller quantity of hot water.

Not only this methylamine salt, but also all of the amine derivatives of benzene-sulphonic acid crystallise in the anhydrous state, a property which they share in common with most ammonium salts of the sulphonic acids. The crystalline salts of the metallic bases with these acids contain, on the contrary, almost invariably one or more molecules of water of crystallisation.

This salt, dried in a vacuum over sulphuric acid, lost no water on heating to 110° .

0.2718 gram of the salt thus dried gave 0.3402 gram of barium sulphate, equal to 0.0467 gram of sulphur, or 17.17 per cent.

S

Calculated for $C_7H_{11}NO_3S$.
16.93

Found.
17.17

Analysis of Sulphonates.—The method used for the sulphur determination in this instance, as well as in the analyses of the salts to be described later, was that indicated some years since by Pearson.¹ This method of oxidising organic substances containing sulphur, which never received the attention it merited, is admirably adapted for the analysis of sulphonates, and certainly surpasses in simplicity and economy the processes now in vogue in our laboratories.

¹ Ztschr. anal. Chem. 9, 271.

As no mention is made of it in the majority of our works on analytical chemistry, we give a brief description of the details of the operation.

The substance to be analysed is mixed in a porcelain dish with potassium chlorate. This mixture is covered by a funnel, the neck of which is bent at a right angle in order to prevent loss by spattering. Nitric acid (1.36 sp. gr.) is gradually added, and the dish gently warmed until complete solution is effected. The excess of acid is driven off by evaporation to dryness, and the sulphuric acid is precipitated from the solution of the residual potassium salts in the ordinary manner.

This method gives almost invariably good results with sulphonates. The only difficulty experienced is an occasional tendency to spatter, and this is obviated by careful attention during the operation. This tendency is more marked in the case of salts with the aromatic amines, and especially in the case of the aniline salt, which on several occasions entered into violent combustion on the addition of the nitric acid.

Dimethylamine benzene-sulphonate, $C_6H_5SO_3H.NH(CH_3)_2$.—The preparation is similar to that of the monamine salt. It crystallises in thin white plates which melt at 110° . This salt is anhydrous, but very deliquescent. It is insoluble in ether, benzene, and carbon disulphide. It is soluble in two and one-half parts of alcohol, in two parts of cold water, and in a very small amount of hot water.

The salt dried in vacuo over sulphuric acid lost no water on heating to 110° .

I. 0.4384 gram of the salt thus dried gave by Pearson's method 0.5065 gram of $BaSO_4$, equal to 0.0695 gram of S or 15.84 per cent.

II. 0.2766 gram gave 0.3175 gram of $BaSO_4$, equal to 0.0436 gram of S or 15.72 per cent.

S	Calculated for $C_8H_{13}NO_3S$.	Found.	
		I.	II.
	15.76	15.84	15.72

Trimethylamine benzene-sulphonate, $C_6H_5SO_3H.N(CH_3)_3$.—The preparation was the same as that of the preceding salts. It is obtained in the form of a mass of white fibrous crystals which are somewhat deliquescent and melt at 88° – 89° . The salt is anhydrous. It is insoluble in ether, benzene, and carbon disulphide. It is

soluble in its own weight of alcohol and of cold water, and is very soluble in hot water.

The salt dried in vacuo over sulphuric acid lost no water on heating to 110°.

0.1687 gram of the salt thus dried gave by Pearson's method 0.1762 gram of BaSO_4 , equal to 0.0242 gram of S or 14.35 per cent.

	Calculated for $\text{C}_9\text{H}_{10}\text{NO}_3\text{S}$.	Found.
S	14.75	14.35

Ethylamine benzene-sulphonate, $\text{C}_6\text{H}_5\text{SO}_3\text{H} \cdot \text{NH}_2\text{C}_2\text{H}_5$.—The preparation is similar to that of the methyl salts. It is obtained in the form of a fibrous mass of white crystals which are anhydrous and melt at 92°. The salt is insoluble in ether, benzene, and carbon disulphide. It is soluble in its own weight of alcohol or cold water, and very soluble in hot water.

The salt dried in vacuo over sulphuric acid lost no water on heating to 110°.

I. 0.5239 gram of the salt thus dried gave 0.5977 gram of BaSO_4 , equal to 0.082 gram of S or 15.51 per cent.

II. 1.0646 grams gave 1.2283 grams BaSO_4 , equal to 0.1687 gram S or 15.85 per cent.

III. 0.9497 gram gave by Will and Varrentrapp's method 0.0632 gram of N, equal to 6.65 per cent.

	Calculated for $\text{C}_8\text{H}_{13}\text{NO}_3\text{S}$.	I.	Found.	II:
N	6.89	6.65		...
S	15.76	15.85		15.51

Diethylamine benzene-sulphonate, $\text{C}_6\text{H}_5\text{SO}_3\text{H} \cdot \text{NH}(\text{C}_2\text{H}_5)_2$.—This salt is prepared by adding the pure amine to the concentrated solution of the acid. On concentration it crystallises in long, colorless, anhydrous prisms which are not very deliquescent. The melting point is 139°. It is insoluble in ether, benzene, and carbon disulphide. It is soluble in 4½ parts of alcohol, 1½ parts of cold water, and less than 1 part of hot water.

The salt dried in vacuo over sulphuric acid lost no water on heating to 110°.

I. 0.6791 gram of the salt thus dried gave 0.6758 gram of BaSO_4 , equal to 0.0928 gram of S or 13.66 per cent.

II. 0.4904 gram of the salt gave 0.4912 gram of BaSO_4 , equal to 0.0674 gram of S or 13.75 per cent.

S	Calculated for $C_{10}H_{17}NO_2S$.	Found.	
		I.	II.
	13.85	13.66	13.75

Triethylamine benzene-sulphonate, $C_6H_5SO_3H.N(C_2H_5)_3$.—Preparation similar to that of the preceding salt. It crystallises in the form of rhombic plates which are anhydrous, but very deliquescent. Melting point 120° – 121° . It is insoluble in ether, benzene, and carbon disulphide. It is soluble in $1\frac{1}{2}$ parts of alcohol or cold water, and is very soluble in hot water.

The salt dried in vacuo over sulphuric acid lost no water on heating to 110° .

0.5248 gram of the salt thus dried gave 0.4785 gram of $BaSO_4$, equal to 0.657 gram of S or 12.51 per cent.

S	Calculated for $C_{12}H_{19}NO_2S$.	Found.	
		I.	II.
	12.45		12.51

Isobutylamine benzene-sulphonate, $C_6H_5SO_3H.NH_2.CH_2.CH(CH_3)_2$.—Preparation similar to that of the preceding salts. The salt crystallises in slender white prisms which are anhydrous and but slightly deliquescent. It melts at 132° . It is insoluble in ether, benzene, and carbon disulphide. It is soluble in 1 part of alcohol, 2 parts of cold water, and 1 part of hot water.

The salt dried in vacuo over sulphuric acid lost no water on heating to 110° .

I. 0.3964 gram of the salt thus dried gave 0.4102 gram of $BaSO_4$, equal to 0.0563 gram of S or 14.2 per cent.

II. 0.459 gram of the salt gave 0.4745 gram of $BaSO_4$, equal to 0.0651 gram of S or 14.2 per cent.

S	Calculated for $C_{10}H_{17}NO_2S$.	Found.	
		I.	II.
	13.86	14.2	14.2

Isoamylamine benzene-sulphonate, $C_6H_5.SO_3H.NH_2.C_5H_{11}$.—Preparation similar to that of the methyl salts. The salt crystallises in thin white plates which are anhydrous, but very deliquescent. It melts at 107° . It is insoluble in ether, benzene, and carbon disulphide. It is soluble in its own weight of cold water or alcohol, and very soluble in hot water.

The salt dried in vacuo over sulphuric acid lost no water on heating to 110° .

0.3079 gram of the salt thus dried gave 0.2867 gram of BaSO_4 , equal to 0.0393 gram of S or 12.78 per cent.

	Calculated for $\text{C}_{11}\text{H}_{13}\text{NO}_3\text{S}$.	Found.
S	13.06	12.78

Aniline benzene-sulphonate, $\text{C}_6\text{H}_5\text{SO}_3\text{H} \cdot \text{NH}_2\text{C}_6\text{H}_5$.—This salt was prepared by adding a very concentrated solution of the acid to aniline. A precipitate was formed which, however, readily dissolved on warming. This solution on cooling deposits the crystals in the form of very fine silky white needles, anhydrous and not deliquescent. The salt melts at 235° – 237° , undergoing slight decomposition at the same time. It is insoluble in benzene, carbon disulphide, and cold ether, but dissolves slightly in hot ether. It is soluble in 8 parts of alcohol or cold water, and in 5 parts of hot water.

The salt dried in vacuo over sulphuric acid lost no water on heating to 110° .

I. 0.1703 gram of the salt thus dried gave 0.15 gram of BaSO_4 , equal to 0.0206 gram of S or 12.09 per cent.

II. 0.17 gram of the salt gave 0.15 gram of BaSO_4 , equal to 0.0206 gram of S or 12.11 per cent.

III. 0.1765 gram of the salt gave 0.1577 gram of BaSO_4 , equal to 0.0216 gram of S or 12.12 per cent.

	Calculated for $\text{C}_{13}\text{H}_{13}\text{NO}_3\text{S}$.	I.	Found. II.	III.
S	12.74	12.09	12.11	12.12

As already mentioned, the determination of the sulphur in this aniline salt was less simple than in the other cases. The addition of nitric acid to the mixture of the salt and potassium chlorate always occasioned a violent reaction, accompanied by spattering and even combustion, during which probably a slight loss occurred, thus accounting for the low results in all the analyses.

This salt was prepared by Gericke¹ by dropping aniline in a warm solution of benzene sulphonic acid. He obtained long, lustrous, silky needles which crystallised in radial groups and which had a reddish color. The salt was easily soluble in water and alcohol, scarcely soluble in ether. He found the melting point to be 201° , but made no analysis.

¹ Ann. Chem. (Liebig) **100**, 217.

The statement with regard to the color and melting point would indicate the presence of impurities in Gericke's product.

Diphenylamine benzene-sulphonate, $C_6H_5SO_3H \cdot NH(C_6H_5)_2$.—

This salt was prepared by adding the concentrated solution of the acid to an alcoholic solution of diphenylamine. The crystals separate out on driving off the alcohol. The salt crystallises in fibrous masses of needles which are anhydrous and of a light bluish gray color. It melts at 115° – 117° . It is insoluble in ether and carbon disulphide. It is soluble in 65 parts of benzene and in four parts of alcohol. It is decomposed by water.

The salt dried in vacuo over sulphuric acid lost no weight on heating to 110° .

0.479 gram of the salt thus dried gave 0.3272 gram of $BaSO_4$, equal to 0.0449 gram of S or 9.59 per cent.

S	Calculated for $C_{18}H_{17}NO_3S$.	Found.
	9.60	9.59

Orthotoluidine benzene-sulphonate, $C_6H_5SO_3H \cdot NH_2C_6H_4$.—

This salt was likewise obtained by adding the aqueous solution of the acid to an alcoholic solution of o-toluidine. The precipitate obtained on driving off the alcohol was dissolved in hot benzene, and the salt crystallised readily on allowing the solution to cool. The crystals form a mass of wool-like filaments, are anhydrous, and possess a slight reddish tinge. The salt melts at 137° . It is insoluble in carbon disulphide and cold benzene. It is soluble in 30 parts of cold water, 2 parts of hot water, $1\frac{1}{2}$ parts of alcohol, 40 parts of hot benzene, and very slightly soluble in ether.

The salt dried in vacuo over sulphuric acid lost no water on heating to 110° .

I. 0.5014 gram of the salt thus dried gave 0.4509 gram of $BaSO_4$, equal to 0.0621 gram of S or 12.34 per cent.

II. 0.5455 gram of the salt gave 0.4969 gram of $BaSO_4$, equal to 0.0682 gram of S or 12.39 per cent.

S	Calculated for $C_{13}H_{13}NO_3S$.	I.	Found.	II.
	12.08	12.34		12.39

α -Naphthylamine benzene-sulphonate, $C_6H_5SO_3H \cdot NH_2C_{10}H_7$.—

Preparation similar to that of the preceding salt. It crystallises in very fine needles which assume a radial structure, are anhydrous,

and possess a slight grayish tint. It melts at 225° with slight decomposition. It is insoluble in ether, benzene, carbon disulphide, and cold water. It is soluble in 30 parts of alcohol and 5 parts of hot water.

The salt dried in vacuo over sulphuric acid lost no water on heating to 110° .

I. 0.1839 gram of the salt thus dried gave 0.1416 gram of BaSO_4 , equal to 0.0194 gram of S or 10.57 per cent.

II. 0.2355 gram of the salt gave 0.1936 gram of BaSO_4 , equal to 0.0265 gram of S or 10.86 per cent.

S	Calculated for	Found.	
	$\text{C}_{16}\text{H}_{11}\text{NO}_2\text{S}$.	I.	II.
	10.63	10.57	10.86

Dimethylaniline, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$, and *methyldiphenylamine*, $(\text{C}_6\text{H}_5)_2\text{NCH}_3$, were also treated with benzene-sulphonic acid. In both cases an alcoholic solution of the amine was added to the aqueous solution of the acid, and the alcohol was driven off. Although both united apparently with the acid, still it was impossible to obtain crystalline salts, even by previous concentration to a temperature of 150° . The syrupy products were also kept for some time in a freezing mixture of ice and salt without, however, giving indications of crystallisation.

XXXV.—ON SOME NEW METALLIC SALTS OF BENZENE-SULPHONIC ACID.

BY T. H. NORTON AND T. W. SCHMIDT.

The following salts were prepared in connection with the general study of the sulphonic acids already mentioned.

The only compounds formed by the union of metallic bases with benzene-sulphonic acid, thus far prepared and analysed, are the barium, copper, zinc, and silver salts. We have increased this number by the addition of the cadmium, manganese, nickel, cobalt, and mercurous salts. The material used in all these preparations was a concentrated solution of barium benzene-sulphonate, obtained as indicated in the early part of the preceding paper.

Cadmium benzene-sulphonate, $(\text{C}_6\text{H}_5\text{SO}_3)_2\text{Cd} + 7\text{H}_2\text{O}$.—A concentrated solution of cadmium sulphate was carefully added to the

solution of barium benzene-sulphonate until barium sulphate was no longer precipitated. The filtered solution of cadmium sulphate was concentrated and allowed to crystallise. This salt crystallises in thin white leaflets containing 7 molecules of water of crystallisation. The water of crystallisation is lost below 100° , the translucent crystals becoming opaque. At 110° they undergo decomposition. They are soluble in two parts of hot water, four and a half parts of cold water, eight parts of alcohol, and twenty-five parts of ether.

Analysis: 1.9677 grams of the salt dried to constant weight at 40° , lost on heating to 100° , 0.4561 gram H_2O , or 23.12 per cent.

	Calculated for $Cd(C_6H_5SO_3)_2 + 7H_2O$.	Found.
H_2O	22.86	23.12

I. 0.3571 gram of the salt dried to constant weight at 100° gave 0.1047 gram of CdO , equal to 0.0917 gram of Cd or 25.75 per cent.

II. 0.4213 gram of the anhydrous salt gave 0.1232 gram of CdO , equal to 0.1078 gram of Cd , or 25.92 per cent.

III. 0.3723 gram of the anhydrous salt gave 0.3946 gram of $BaSO_4$, equal to 0.0542 gram of S or 14.56 per cent.

	Calculated for $CdC_{12}H_{10}S_2O_4$.	I.	Found.	II.
Cd	26.29	25.75		25.92
S	15.02	14.56		...

Manganese benzene-sulphonate, $(C_6H_5SO_3)_2Mn + 6H_2O$.—A concentrated solution of manganese sulphate was added to the solution of barium sulphonate to the point of complete precipitation of barium sulphate. On concentrating the filtered solution of manganese sulphonate it was crystallised in the form of thin white scales with a mother of pearl lustre. The crystals contain six molecules of water of crystallisation, which are lost below 100° , when the translucent crystals become opaque. At 130° the salt begins to decompose, turning first gray and then black. The crystals are soluble in 20 parts of ether and six parts of alcohol, while one part of water dissolves four parts of the crystals.

Analysis: 2.9396 grams of the crystals dried to constant weight at 40° , lost on heating to 100° , 0.6532 gram H_2O , equal to 22.24 per cent.

	Calculated for $Mn(C_6H_5SO_3)_2 + 6H_2O$.	Found.
H_2O	22.63	22.24

I. 0.8156 gram of the anhydrous salt dried to constant weight at 100° gave 0.1753 gram of Mn_2O_4 , equal to 0.1263 gram Mn or 14.40 per cent.

II. 0.4375 gram of the same substance gave 0.0956 gram of Mn_2O_4 , equal to 0.0689 gram Mn or 14.68 per cent.

III. 0.8375 gram of the same gave 1.0035 grams BaSO_4 , equal to 0.1377 gram S or 16.46 per cent.

IV. 0.8653 gram of the same gave 1.0806 grams BaSO_4 , equal to 0.1479 gram S or 17.14 per cent.

	Calculated for $\text{Mn}(\text{C}_6\text{H}_5\text{SO}_3)_2$.	Found.	
		I.	II.
Mn	14.90	14.40	14.68
S	17.34	16.46	17.14

Nickel benzene-sulphonate, $(\text{C}_6\text{H}_5\text{SO}_3)_2\text{Ni} + 6\text{H}_2\text{O}$.—The preparation was similar to that of the preceding salts, use being made of a concentrated solution of nickel sulphate. Nickel benzene-sulphonate crystallises readily in large well defined octagonal plates, which are colorless by transmitted light, and a delicate green by reflected light. It contains six molecules of water of crystallisation, which are lost at 100° , while at the same time the color becomes a dingy yellow. The anhydrous salt is extremely deliquescent. It decomposes at 165° . It is soluble in two parts of hot water, eight parts of cold water, seventeen parts of alcohol, and twenty-two parts of ether.

Analysis: I. 0.4938 gram of the crystallised salt dried to constant weight at 40° , lost on heating to 100° , 0.1113 gram H_2O , or 22.54 per cent.

II. 0.8573 gram of the same gave 0.1317 gram of NiO , equal to 0.1034 gram Ni or 12.08 per cent.

III. 0.9242 gram of the same gave 0.1488 gram of NiO , equal to 0.117 gram Ni or 12.69 per cent.

IV. 0.4632 gram of the same gave 0.4401 gram of BaSO_4 , equal to 0.0604 gram S or 13.0 per cent.

V. 1.3825 grams of the same gave 1.2968 grams of BaSO_4 , equal to 0.1651 gram S or 12.88 per cent.

	Calculated for $\text{Ni}(\text{C}_6\text{H}_5\text{SO}_3)_2 + 6\text{H}_2\text{O}$:	Found.	
		I.	II.
H_2O	22.46	22.54	...
Ni	12.27	12.08	12.69
S	13.30	13.00	12.88

Cobalt benzene-sulphonate, $\text{Co}(\text{C}_6\text{H}_5\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$.—This salt was prepared in the same way as the preceding compounds, a concentrated solution of cobalt sulphate being used. The crystals are obtained in the form of octagonal plates—thicker than in the case of the nickel salt—colorless by transmitted light, and light red by reflected light. They contain 6 molecules of water of crystallisation, which are lost at 100° , the color at the same time becoming purple. Decomposition takes place at 185° . The crystallised salt dissolves in 3 parts of hot water, 11 parts of cold water, 22 parts of alcohol, and 34 parts of ether. The anhydrous salt is very deliquescent.

Analysis: I. 0.4810 gram of the crystallised salt dried to constant weight at 40° , lost on heating to 100° , 0.1076 gram of H_2O , or 22.20 per cent.

II. 0.7665 gram of the same gave 0.1223 gram of CoO , equal to 0.0961 gram of Co or 12.55 per cent.

III. 0.8511 gram of the same gave 0.1395 gram of CoO , equal to 0.1096 gram of Co or 12.89 per cent.

IV. 1.2995 grams of the same gave 1.1893 grams of BaSO_4 , equal to 0.1633 gram of S or 12.56 per cent.

V. 1.1205 grams of the same gave 1.0538 grams of BaSO_4 , equal to 0.1448 gram of S or 12.90 per cent.

	Calculated for $\text{Co}(\text{C}_6\text{H}_5\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$.	I.	Found. II.
H_2O	22.54	22.20	...
Co	12.27	12.55	12.89
S	13.30	12.56	12.90

Mercurous benzene-sulphonate, $\text{C}_6\text{H}_5\text{SO}_3\text{Hg}$.—This salt was precipitated in the form of an amorphous mass on the addition of a solution of mercurous nitrate to a solution of barium benzene-sulphonate. It is anhydrous and of a yellowish white color. It decomposes at 185° , decomposition being indicated by the appearance of small globules of mercury. It is insoluble in water and alcohol, and very slightly soluble in ether.

Analysis: I. 0.443 gram of the salt dried to constant weight at 40° gave 0.2911 gram of HgS , equal to 0.2518 gram of Hg or 56.83 per cent.

II. 0.6266 gram of the same gave 0.4176 gram of HgS , equal to 0.3591 gram of Hg or 56.60 per cent.

III. 1.4031 grams of the same gave 0.8815 gram of BaSO_4 , equal to 0.1218 gram of S or 8.68 per cent.

IV. 1.5181 grams of the same gave 0.9625 gram of BaSO_4 , equal to 0.1322 gram of S or 8.70 per cent.

	Calculated for $\text{HgC}_6\text{H}_5\text{SO}_3$.	Found.	
		I.	II.
Hg	56.01	56.83	56.60
S	8.96	8.68	8.70

With regard to the amount of water of crystallisation in the first four salts described, it may be mentioned that with the exception of the cadmium salt, all possess the same number of molecules of water, viz. $6\text{H}_2\text{O}$, that has been found previously in the copper and zinc salts of benzene-sulphonic acid.

XXXVI.—ON THE AMINE SALTS OF PARA-TOLUENE-SULPHONIC ACID.

BY T. H. NORTON AND A. H. OTTEN.

The matter contained in this paper was prepared in connection with the general study of sulphonic acids alluded to in the two preceding articles.

The para-toluene-sulphonic acid used in the preparation of the salts to be described was made according to the directions of Chruschow,¹ viz., by adding concentrated sulphuric acid, drop by drop, to boiling toluene. The best results were obtained by using equal weights of hydrocarbon and acid. The sulphonic acid was purified in the same manner as indicated in paper XXXIV for the preparation of the benzene-sulphonic acid, viz., neutralisation with barium carbonate and careful precipitation of the barium by sulphuric acid.

As the melting point of the crystallised para-toluene-sulphonic acid has not been hitherto ascertained, it was carefully determined and found to be 92° . On adding amines to this acid, as a rule stable salts are formed, most of which are soluble in water. Those obtained from the amines of the aromatic series crystallise easily in well defined forms, while the amines of the normal paraffin series yield salts which, on account of their great solubility, are generally obtained in radial crystalline masses or rosettes. The former class are likewise less soluble in water and more soluble in alcohol than the

¹ Ber. d. chem. Ges. 7, 1167.

latter. A third difference is noticed in their deportment towards test paper. The former have a pronounced acid reaction, while the latter are neutral or alkaline. All of the salts are, like ammonium para-toluene-sulphonate, destitute of water of crystallisation.

In the determinations of sulphur, Pearson's method (see paper XXXIV) was used exclusively, and with highly satisfactory results.

Methylamine Para-toluene-sulphonate, $C_7H_7SO_3H.NH_2CH_3$.—A 33 per cent. aqueous solution of methyl-amine was added to the concentrated aqueous solution of para-toluene-sulphonic acid. On concentration the salt crystallises in pale rose-colored rosettes which have a mother-of-pearl lustre, are anhydrous, and melt at 125° . The salt is insoluble in carbon disulphide, ether, and benzene. It dissolves in 10 parts of alcohol, $1\frac{1}{2}$ parts of water at 23° , and less than 1 part of water at 100° . It is very deliquescent.

The salt dried to constant weight over sulphuric acid in vacuo lost no weight on heating to 110° .

I. 0.2334 gram of the salt thus dried gave 0.2639 gram of $BaSO_4$, equal to 0.0362 gram of S or 15.53 per cent.

II. 0.2063 gram of the dried salt gave 0.2361 gram of $BaSO_4$, equal to 0.0324 gram of S or 15.71 per cent.

S	Calculated for $C_8H_{10}O_3SN$.	Found.	
	I.	II.	
	15.76	15.53	15.71

Dimethylamine Para-toluene-sulphonate, $C_7H_7SO_3H.NH(CH_3)_2$.—Preparation similar to that of the preceding salt. It crystallises in white fibrous masses with a feathery appearance, is anhydrous, melts at 78° , and is very deliquescent. It is insoluble in carbon disulphide, ether, and benzene. It dissolves in 2 parts of alcohol, and in one part of water at 23° . The salt dried to constant weight over sulphuric acid in vacuo lost no weight on heating to 110° .

I. 0.2333 gram of the salt thus dried gave 0.2458 gram of $BaSO_4$, equal to 0.0337 gram of S or 14.46 per cent.

II. 0.2304 gram of the dry salt gave 0.2452 gram of $BaSO_4$, equal to 0.0336 gram of S or 14.61 per cent.

S	Calculated for $C_9H_{12}O_3SN$.	Found.	
	I.	II.	
	14.75	14.46	14.61

Trimethylamine Para-toluene-sulphonate, $C_7H_7SO_3H.N(CH_3)_3$.—Preparation similar to that of the preceding salts. It crystallises in pale green rosettes which melt at 92° , are anhydrous,

and are very deliquescent. The crystals are insoluble in carbon disulphide, ether, and benzene. They are soluble in 4.3 parts of alcohol and 3.7 parts of cold water.

The salt dried to constant weight over sulphuric acid in vacuo lost no weight on heating to 110° .

I. 0.2176 gram of the salt thus dried gave 0.2146 gram of BaSO_4 , equal to 0.0294 gram of S or 13.54 per cent.

II. 0.2195 gram of the dry salt gave 0.222 gram of BaSO_4 , equal to 0.0304 gram of S or 13.89 per cent.

S	Calculated for $\text{C}_{10}\text{H}_{11}\text{O}_2\text{SN}$.	Found.	
		I.	II.
	13.85	13.54	13.89

Ethylamine Para-toluene-sulphonate, $\text{C}_7\text{H}_7\text{SO}_3\text{H.NH}_2\text{C}_2\text{H}_5$. — Preparation similar to that of the methyl salts. It crystallises in white radial masses which are anhydrous and very deliquescent. The melting point is 111° . The salt is insoluble in carbon disulphide, ether, and benzene. It is soluble in 7.7 parts of alcohol, in one half its weight of water at 100° , and in less than its weight of water at 23° .

The salt dried to constant weight over sulphuric acid in vacuo lost no weight on heating to 110° .

I. 0.503 gram of the salt thus dried gave 0.5309 gram of BaSO_4 , equal to 0.0729 gram of S or 14.49 per cent.

II. 0.3371 gram of the dry salt gave 0.3495 gram of BaSO_4 , equal to 0.048 gram of S or 14.27 per cent.

S	Calculated for $\text{C}_9\text{H}_{10}\text{O}_2\text{SN}$.	Found.	
		I.	II.
	14.75	14.49	14.27

Diethylamine Para-toluene-sulphonate, $\text{C}_7\text{H}_7\text{SO}_3\text{H.NH}(\text{C}_2\text{H}_5)_2$. — Diethylamine was added to the solution of the sulphonic acid until the liquid was neutralised. On concentration the salt crystallises in white rosettes or warts which are anhydrous and very deliquescent. The melting point is 88° . The crystals are insoluble in carbon disulphide, ether, and benzene. They are soluble in 3.7 parts of alcohol, and in 1 part of water at 23° .

The salt dried to constant weight over sulphuric acid in vacuo lost no weight on heating to 110° .

I. 0.4423 gram of the salt thus dried gave 0.4157 gram of BaSO_4 , equal to 0.057 gram of S or 12.89 per cent.

II. 0.372 gram of the dry salt gave 0.3595 gram of BaSO_4 , equal to 0.0499 gram of S or 13.27 per cent.

S	Calculated for $\text{C}_{11}\text{H}_{19}\text{O}_3\text{SN}$.	Found.	
	13.06	I.	II.
		12.89	13.27

Triethylamine Para-toluene-sulphonate, $\text{C}_7\text{H}_7\text{SO}_3\text{H.N}(\text{C}_2\text{H}_5)_3$.—Preparation similar to that of the preceding salt. It crystallises in very deliquescent fibrous white masses. It is anhydrous and melts at 65° . The fused mass becomes green on heating to 110° . The crystals are insoluble in carbon disulphide, ether, and benzene. They dissolve in 2 parts of alcohol and 0.6 parts of water at 22° . The salt dried to constant weight over sulphuric acid in vacuo lost no weight on heating to 110° .

I. 0.3531 gram of the salt thus dried gave 0.3087 gram of BaSO_4 , equal to 0.0424 gram of S or 12.00 per cent.

II. 0.3395 gram of the dry salt gave 0.3007 gram of BaSO_4 , equal to 0.0412 gram of S or 12.16 per cent.

S	Calculated for $\text{C}_{11}\text{H}_{23}\text{O}_3\text{SN}$.	Found.	
	11.72	I.	II.
		12.00	12.16

Aniline Para-toluene-sulphonate, $\text{C}_7\text{H}_7\text{SO}_3\text{H.NH.C}_6\text{H}_5$.—This salt was obtained by adding aniline to an alcoholic solution of the sulphonic acid. It forms long glistening white needles which assume a mother-of-pearl lustre on heating to 110° . The crystals are anhydrous, possess an acid reaction, and melt at 223° . They are insoluble in carbon disulphide, ether, and benzene. They dissolve in 5.2 parts of alcohol, 2 parts of water at 100° , and 8 parts of water at 23° .

The salt dried to constant weight over sulphuric acid in vacuo lost no weight on heating to 110° .

I. 0.3062 gram of the salt thus dried gave 0.2859 gram of BaSO_4 , equal to 0.0392 gram of S or 12.82 per cent.

II. 0.1815 gram of the dry salt gave 0.1662 gram of BaSO_4 , equal to 0.0228 gram of S or 12.63 per cent.

S	Calculated for $\text{C}_{13}\text{H}_{15}\text{O}_3\text{SN}$.	Found.	
	13.28	I.	II.
		12.82	12.63

Diphenylamine Para-toluene-sulphonate, $\text{C}_7\text{H}_7\text{SO}_3\text{H.NH}(\text{C}_6\text{H}_5)_2$.—Diphenylamine was added to the ethereal solution of the sul-

phonic acid to saturation. The salt crystallises in fine needles of a greenish gray color, which are anhydrous and melt at 64° . The fused salt turns deep green at 225° and decomposes at 255° . The salt is insoluble in carbon disulphide and benzene. It dissolves in 2.5 parts of alcohol and in 31 parts of ether. It is decomposed by water.

The salt dried to constant weight over sulphuric acid in vacuo lost no weight on heating to 110° .

I. 0.2013 gram of the salt thus dried gave 0.1397 gram of BaSO_4 , equal to 0.0191 gram of S or 9.53 per cent.

II. 0.2053 gram of the dry salt gave 0.1405 gram of BaSO_4 , equal to 0.0192 gram of S or 9.39 per cent.

S	Calculated for $\text{C}_{19}\text{H}_{19}\text{O}_3\text{SN}$.	Found.	
	9.38	I. 9.53	II. 9.39

Ortho-toluidine Para-toluene-sulphonate, $\text{C}_7\text{H}_5\text{SO}_3\text{H.NH}_2\text{C}_6\text{H}_3$.—This salt is obtained by adding ortho-toluidine to an alcoholic solution of the sulphonic acid. It crystallises on concentration in long narrow prisms of a light purplish color, which are anhydrous and melt at 180° .

The salt dried to constant weight over sulphuric acid in vacuo lost no weight on heating to 110° .

I. 0.304 gram of the salt thus dried gave 0.2588 gram of BaSO_4 , equal to 0.0355 gram of S or 11.69 per cent.

II. 0.3017 gram of the dry salt gave 0.2446 gram of BaSO_4 , equal to 0.0335 gram of S or 11.13 per cent.

S	Calculated for $\text{C}_{14}\text{H}_{17}\text{O}_3\text{SN}$.	Found.	
	11.47	I. 11.69	II. 11.13

α -Naphthylamine Para-toluene-sulphonate, $\text{C}_7\text{H}_5\text{SO}_3\text{H.NH}_2(\text{C}_{10}\text{H}_7)$.— α -Naphthylamine was added to an alcoholic solution of the sulphonic acid. On concentration the salt crystallises in anhydrous needle-like prisms of a grayish color. They turn purplish on heating and melt at 239° . The salt is insoluble in carbon disulphide, benzene, ether, and water, but dissolves in 20 parts of alcohol.

The salt dried over sulphuric acid in vacuo to constant weight lost no weight on heating to 110° .

I. 0.2345 gram of the salt thus dried gave 0.1747 gram of BaSO_4 , equal to 0.0239 gram of S or 10.23 per cent.

II. 0.2604 gram of the dry salt gave 0.191 gram of BaSO_4 , equal to 0.0262 gram of S or 10.07 per cent.

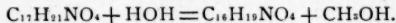
S	Calculated for	Found.	
	$\text{C}_{17}\text{H}_{17}\text{O}_3\text{SN}$.	I.	II.
	10.16	10.23	10.07

Reaction with dimethyl-aniline.—An aqueous solution of para-toluene sulphonic acid was saturated with an alcoholic solution of dimethyl-aniline. The mixture was concentrated on the water-bath, but no crystals appeared. The viscous liquid was then heated to 150° to drive off the last traces of water, and, although it was afterward kept for several days in a freezing mixture, no crystals could be obtained.

SOME HIGHER HOMOLOGUES OF COCAINE.¹

BY FREDERICK G. NOVY.

The well known alkaloid cocaine is the methyl ester of benzoyl-ecgonine. This latter substance does not occur ready formed in nature, but it is obtained by the saponification of cocaine. The process is one of simple hydration; the alkaloid splitting up into benzoyl-ecgonine and methyl alcohol according to the equation:



On heating benzoyl-ecgonine with methyl iodide and methyl alcohol it is readily converted back into cocaine. Similarly, when heated with any one of the higher alkyl iodides the corresponding homologue of cocaine is obtained.

The ethyl ester of benzoyl-ecgonine was first prepared and partially studied by W. Merck in 1885. He obtained it by heating benzoyl-ecgonine with ethyl iodide and ethyl alcohol in a sealed tube for 8 hours at 100° . This method with slight modifications was the one used in the preparation of this and the succeeding homologues. Several grams of benzoyl-ecgonine were heated about 5 hours at 95° with a quantity of ethyl iodide slightly in

¹ Read at the New York meeting of the American Association for the Advancement of Science.

excess of the theoretically required amount, and some absolute alcohol. When cold the tube was opened and the contents transferred to a small evaporating dish. The alcohol and excess of ethyl iodide was driven off at a low heat on the water-bath. The yellowish syrup was taken up with warm water, filtered, and the filtrate after being made alkaline with sodium carbonate was extracted with ether. The ether solution on evaporation left a yellowish crystalline mass. This was further purified by dissolving it in dilute hydrochloric acid; the acid solution was filtered, and the filtrate extracted repeatedly with ether to remove the coloring matter. The colorless solution thus obtained was now made alkaline with sodium carbonate and again extracted with ether. On evaporation of the ether solution the alkaloid was obtained in the form of delicate white silky crystals, arranged in sheaves or stellate groups. By recrystallisation from alcohol the substance was obtained in large clear monoclinic prisms resembling those of cocaine. Analysis of the platinum salt gave results agreeing with the formula $[C_{16}H_{15}(C_2H_5)NO_4 \cdot HCl]_2PtCl_6$.

Ladenburg has suggested for this compound the name cocethyline. And according to this nomenclature the next higher member would be cocpropylene, etc. I have preferred to use names which suggest the chemical constitution of the substance. Thus, since cocaine is the methyl ester of benzoyl-ecgonine, it can be named *methyl-benzoyl-ecgonine*. The succeeding homologues accordingly become *ethyl-benzoyl-ecgonine*, *propyl-benzoyl-ecgonine*, etc.

The crystals of ethyl-benzoyl-ecgonine melt at 107° – 108° , and solidify again at about 90° . Like cocaine it forms easily crystallisable salts. The hydrochloride crystallises in beautiful colorless needles or prisms. It is readily soluble in water and alcohol, insoluble in ether. Platinum chloride produces in solutions of the hydrochloride a yellow precipitate of splendid glittering rhombic plates. The precipitate is soluble in warm water, from which it recrystallises on cooling. It is also soluble in hydrochloric acid and in warm alcohol.

Gold chloride produces a voluminous yellowish-white precipitate, soluble in warm water, in excess of cold hydrochloric acid, and in alcohol. Phospho-molybdic acid gives a heavy yellowish-white precipitate. Mayer's reagent produces a white precipitate; picric acid, a yellow, readily soluble precipitate; iodine in potassium iodide yields a kermes-brown precipitate; bromine water, a yellow

precipitate soluble in ammonium hydrate; potassium iodide and potassium sulphocyanide produce only a slight cloudiness; mercuric chloride gives a white precipitate which is readily soluble in warm water; stannous chloride also gives a white precipitate; disodic hydric-phosphate produces in concentrated solutions a white precipitate which is soluble in water and in acetic acid.

Hydrobromic acid, iodic acid, ammonium oxalate, ferric chloride, potassic bichromate, give no precipitate; alkalies and alkali carbonates yield a white precipitate which is soluble in large excess.

The alkaloid, as well as its salts, possesses a strong anaesthetic action similar to that of cocaine.

Monobrom-ethyl-benzoyl-ecgonine, $C_{16}H_{19}(C_2H_4Br)NO_4$.—This compound was prepared by heating benzoyl-ecgonine with ethylene bromide and alcohol in a sealed tube for 5 hours at 95° . As in the preparation of the preceding compound the solution was evaporated on the water-bath to drive off the excess of alcohol and ethylene bromide. The syrupy residue was then taken up with water, and after being made alkaline with sodium carbonate was extracted with ether. This on evaporation gave a clear colorless syrup which did not show any sign of crystallisation even after several days.

The free alkaloid, as well as the hydrochloride, has a bitter taste and a strong anaesthetic action. The hydrochloride formed a thick yellowish syrup which showed no tendency to crystallise. When kept for some months over sulphuric acid it solidified to a hard transparent glassy mass, full of cracks but entirely free from crystals. It is readily soluble in water and alcohol, insoluble in ether. Its behavior to reagents is almost identical with that of ethyl-benzoyl-ecgonine.

Propyl-benzoyl-ecgonine, $C_{18}H_{23}(C_3H_7)NO_4$.—This compound was obtained in exactly the same way as the preceding. The benzoyl-ecgonine was heated with propyl iodide and propyl alcohol. The free alkaloid crystallises from ether in fine colorless prisms or radiating silky needles; from alcohol in large transparent flat prisms which melt at 78° – 79.5° , and solidify again at about 65° . The low melting point of this compound and of the following isobutyl derivative deserves special attention. Benzoyl-ecgonine containing four molecules of water melts at 90° – 92° , while cocaine, the methyl derivative, melts at 98° , and the ethyl compound has its melting point at 107° – 108° . Although

the propyl and isobutyl compounds were repeatedly prepared, the melting points were found to be always constant and lower than those of the other homologues. This is perhaps due to a different position of the substituting group in the molecule.

The alkaloid has a very bitter taste and possesses a strong anaesthetic action. The hydrochloride is readily soluble in water and alcohol, insoluble in ether. Ordinarily it is in a syrupy condition, but when kept over sulphuric acid for some time it yields a mass of fine white crystals. With reagents it behaves the same as the preceding.

Disodic hydric phosphate produces in concentrated solutions a white precipitate which is at first amorphous, but soon crystallises, forming long colorless plates often arranged in groups. They are soluble in water and in acetic acid.

Isobutyl-benzoyl-ecgonine, $C_{16}H_{18}(C_6H_5)NO_4$.—The same method of preparation was used for this compound as for the preceding; isobutyl iodide and the corresponding alcohol being employed. The ether solution of the alkaloid on evaporation left a colorless syrup which soon began to crystallise. Recrystallised from alcohol it gave a mass of short colorless prisms which melted at 61° – 62° . They possess an intense bitter taste and strong anaesthetic action.

The hydrochloride solidifies over sulphuric acid to a hard yellowish glassy mass almost free from crystals. It exhibits the same reactions with reagents as cocaine and the other homologues. Potassium iodide and sulphocyanide produce in concentrated solutions a white precipitate.

UNIVERSITY OF MICHIGAN, July, 1887.

ON THE SUPPOSED DISSOCIATION OF ZINC OXIDE, AND THE CONDITION OF THE ATMOSPHERE WITHIN A PLATINUM VESSEL HEATED BY A GAS FLAME.

BY H. N. MORSE AND W. M. BURTON.

Some years ago it was found by one of us that zinc, in the highest state of purity and in considerable quantity, can be prepared by subjecting the metal to fractional distillation in a vacuum.

When the pressure is wholly removed the zinc distills at a temperature apparently not much above its fusing point, while the other metals usually associated with it are, at that temperature, very much more or very much less volatile. The separation of zinc from lead by this method is especially rapid and satisfactory. It seemed desirable, therefore, that a redetermination of the atomic weight of the metal, with the elementary substance as a starting point, should be undertaken.

Of all the methods which have been employed for the purpose, or which suggested themselves as feasible, the determination by means of the oxide appeared to be the most simple and direct, and therefore the best, provided the stability of the oxide at high temperatures could be demonstrated. The details of our work will be published at a later date; but some of the results having a more general interest, we venture to present them now. Having demonstrated that the oxide of zinc does not lose weight when heated for many hours in the muffle furnace to a temperature above that required to fuse steel; moreover, that the platinum crucibles containing the oxide do not exhibit any trace of tarnish after such heating; we turned our attention to a phenomenon which must be familiar to many chemists, namely, that when the oxide of zinc is heated in platinum over a blast lamp, or even over an efficient simple burner without blast, it constantly loses weight.

Axel Erdmann¹ observed, while making a determination of the atomic weight of zinc, that when the oxide is heated in a crucible the platinum becomes coated with a blue tarnish supposed to be an alloy of zinc and platinum. Much later Marignac² noticed the same tarnish upon the platinum when the oxide is heated over the blast lamp; moreover, that there is a manifest distillation of the zinc out of the crucible and a constant loss in weight. This loss he ascribes to *dissociation* of the oxide.

In view of the results of Deville³ relating to the dissociation temperature of water, and of Deville and Troost⁴ relating to the permeability at high temperatures of platinum to hydrogen, it appeared probable to us that the phenomenon is one of *reduction* and not of *dissociation*; that the temperature of the gas flame in parts being above that at which the dissociation of water begins, there is in the flame at the same time free oxygen and free hydro-

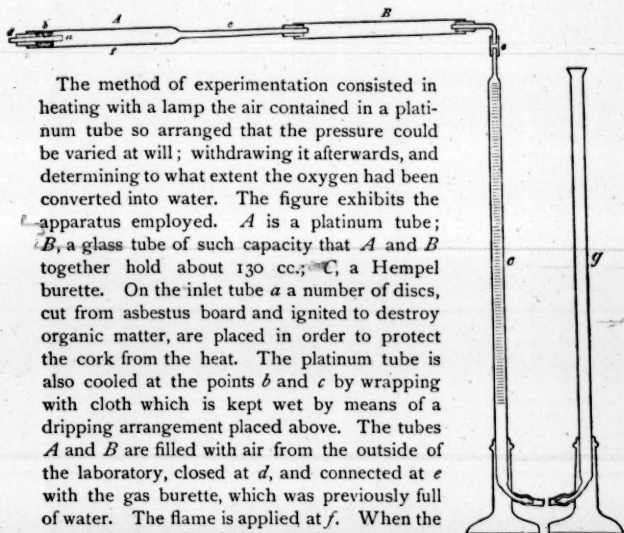
¹ Ann. Chem. (Liebig), **50**, 438.

² Jsb. Chem., 1860, 24.

³ Archives des Sciences Phys. et Nat. (3) **10**, 193.

⁴ Jsb. Chem., 1863, 23.

gen resulting from the dissociation of water previously formed by the combustion of the gas. The result would be an accumulation of free hydrogen on the inside of any platinum vessel heated in the gas flame, due to the more rapid diffusion of hydrogen through heated platinum. Our results have justified this explanation, and make it appear probable that the atmosphere within a platinum vessel heated by such flames as are employed in the laboratory is always a *reducing* atmosphere.



The method of experimentation consisted in heating with a lamp the air contained in a platinum tube so arranged that the pressure could be varied at will; withdrawing it afterwards, and determining to what extent the oxygen had been converted into water. The figure exhibits the apparatus employed. *A* is a platinum tube; *B*, a glass tube of such capacity that *A* and *B* together hold about 130 cc.; *C*, a Hempel burette. On the inlet tube *a* a number of discs, cut from asbestos board and ignited to destroy organic matter, are placed in order to protect the cork from the heat. The platinum tube is also cooled at the points *b* and *c* by wrapping with cloth which is kept wet by means of a dripping arrangement placed above. The tubes *A* and *B* are filled with air from the outside of the laboratory, closed at *d*, and connected at *e* with the gas burette, which was previously full of water. The flame is applied at *f*. When the air within the tubes has attained its maximum expansion, the level of the water in *g* is adjusted according to the pressure which it is desired to maintain in the apparatus. At the end of each ten minute period of heating the tube is allowed to cool down, in order to facilitate the mixing of the portions of the gas in *A*, *B* and *C*. Finally a small glass tube, filled with water and dipping under water in a beaker, is attached at *d*; the gas withdrawn by lowering *g*, and analysed by the method of Hempel.

The substances looked for, and determined when found, were carbon dioxide, oxygen, carbon monoxide, hydrogen, and nitrogen.

The quantity of carbon dioxide found was not in any case in excess of the quantity normally contained in the air, and was, of course, hardly measurable in the ordinary Hempel burette. Carbon monoxide was not found at all. The hydrogen was determined by absorption in palladium sponge, the tube containing it having first been filled with pure nitrogen. The fact that the air did not perceptibly diminish in volume when treated with caustic potassa to withdraw carbon dioxide, proves that no oxides of nitrogen were formed during the heating. Great care was taken in all cases to use only an oxidising flame, and not to allow the internal cone containing the unburned gases to come in contact with the platinum tube. The results obtained are stated in Table I. The percentages of oxygen given represent the proportion of that element which *disappeared* during the heating, and are calculated on the basis that the air contains 20.9 per cent. of oxygen and 79.1 per cent. of nitrogen. The quantities of free hydrogen found are given in cubic centimetres.

TABLE I.

No. of Exp.	Source of Heat.	Time of Heating.	Pressure.	Percent. of total oxygen lost.	Cc. free Hydrogen found.
1	Blast Lamp.	1 Hour.	Atmos. Press. less 30 mm. Merc.	63.07	
2	"	1 "	"	62.08	
3	"	1 "	Atmos. Press.	53.70	
4	"	1 "	"	54.13	
5	"	1 "	At. Pr. + 30 mm. Merc.	48.67	
6	"	2 "	At. Press.	88.49	
7	"	2 "	"	88.53	
8	"	3 "	"	98.14	2.4
9	"	4 "	"	100.00	2.7
10	{ Simple Bun- sen Burner without Blast. }	3 "	"	55.56	
11		6 "	"	81.81	
12		10 "	"	97.00	0.7

In Table II are given the number of cubic centimetres of oxygen burned out in each experiment, also the minimum volume of free hydrogen which must have diffused from the flame into the tube. The calculation is, of course, based on the supposition that the

residual nitrogen is to the oxygen originally mingled with it as 79.1 is to 20.9.

TABLE II.

No. of Exp.	Vol. of O ₂ lost.	Min. vol. of H ₂ .
1	13.75 CC	27.50 CC
2	14.89	29.78
3	11.40	22.80
4	11.41	22.82
5	10.43	20.86
6	21.73	43.46
7	22.28	44.56
8	21.03	2.4 42.06 } 44.46
9	22.75	2.70 45.50 } 48.20
10	12.50	25.00
11	19.80	39.60
12	22.81	0.70 45.62 } 46.32

If we compare the results of Experiments Nos. 1 and 2 with 3 and 4, and with 5, it appears that the diffusion of hydrogen from the flame through platinum is affected by difference in pressure, being greater when the pressure on the inside is diminished. It appears from Experiments Nos. 8 and 12 that when the oxygen has been reduced to a small quantity, both free oxygen and free hydrogen may exist together in the tube.

Experiment No. 9 was undertaken in order to determine whether it is possible wholly to remove the oxygen, and the fact that the volume did not perceptibly decrease when the gas was passed into the phosphorus absorption pipette indicates that it may. But the gas, when it was returned to the burette for measurement, appeared to contain a minute quantity of the white clouds which appear when oxygen is absorbed by phosphorus. To settle this question satisfactorily, finer measuring apparatus and greater precautions against possible diffusion of oxygen from the outside will be required.

That the quantity of free hydrogen found in Experiment No. 9 was not markedly larger than that found in No. 8 is not surprising, because, the tube being hot on all sides, it passes out of the rear wall with nearly the same facility that it enters in front. Moreover,

the connections are necessarily such that free hydrogen would be lost through them. It was our first plan to fill the tube with some gas free from oxygen, and to measure the hydrogen which accumulated in it; but the reflection that free hydrogen was not likely under the circumstances to accumulate with rapidity, and that the quantity found afterwards would be no measure of that which had diffused in during the experiment, led us to select air instead.

Our results appear to explain sufficiently the cause of the constant loss in weight when the oxide of zinc is heated in platinum over a gas flame, and to make it extremely probable that the atmosphere within any platinum vessel heated by any gas flame whatever will receive free hydrogen. They also explain the origin of many of those tarnishes and sublimates which the analytical chemist so often finds on the inside of his crucible after heating substances supposed to be non-volatile. Since only the so-called oxidising portions of the flames were allowed to come in contact with the platinum, the free hydrogen which diffused through the metal must have been produced by the dissociation of water. Whether this dissociation is due solely to the high temperature of the flame, or in part to the influence of the platinum itself, is a question for further investigation. It appears not improbable that the very different rates of diffusion of hydrogen and oxygen through platinum at high temperatures may be a cause of the dissociation of the highly heated water vapor, just as different rates of diffusion through liquids of the constituents of some compounds may determine their decomposition while undergoing solution.

The idea suggests itself in this connection that the oxidising effect of the outer blow-pipe flame may be due to the oxygen derived from dissociating water, rather than from the excess of oxygen blown into it. Such a supposition accords well with the common experience that the best oxidising effects are produced by the *hottest* flame, and not by the flame into which a large excess of air is pumped. A molecule of water heated to a temperature at which it becomes unstable would doubtless be a more active oxidising agent than a molecule of free oxygen.

A METHOD FOR THE SEPARATION AND DETERMINATION OF BORIC ACID.

BY H. N. MORSE AND W. M. BURTON.

The indicator, tropaeolin *OO*, not being sensitive to boric, carbonic, and silicic acids, or to their salts, it is practicable to liberate exactly one or all of these acids in any mixture of inorganic substances. In other words, if to a solution containing silicates, carbonates, and borates, and any other inorganic salts or hydroxides, we add tropaeolin and then dilute sulphuric acid, we shall not obtain an acid reaction until all of the silicic, carbonic, and boric acids have been liberated. In the meantime, any oxides or hydroxides which were present will have been converted into sulphates, so that the mixture will finally consist of neutral salts, water, silicic, carbonic, and boric acids. If we now add to this mixture a sufficient quantity of dehydrated copper sulphate, the water will be absorbed and the silicic acid dehydrated. The mass will then consist of neutral salts, silica, and boric acid, of which only the boric acid is soluble in absolute alcohol. These facts enable us to separate boric acid with great exactness from nearly all other forms of inorganic matter. The only classes of salts known to us at present which are at all likely to interfere with such a separation, are the chlorides and the compounds of iron, but both of these may be readily removed before the acids in question are liberated. The boric acid thus separated may be determined as a meta-borate of calcium, magnesium, or barium. We prefer the last form; because a mixture of carbonate and meta-borate of barium, being neither markedly hygroscopic nor capable of absorbing carbon dioxide, can be brought to a constant weight more readily than one containing the oxide of calcium or magnesium. Moreover, the use of barium enables us to employ a standard solution of hydroxide to receive the alcoholic extract of boric acid, thus saving the labor of bringing the absorbing material itself to a constant weight.

The Reagents.

1. An aqueous solution of tropaeolin *OO*.
2. A standard solution of sulphuric acid of such strength that one cubic centimeter of it is equivalent to twenty milligrams of barium carbonate.

3. A solution of barium hydroxide approximately equivalent to the sulphuric acid. This is prepared by agitating the solid commercial hydroxide with a little cold water, filtering, and washing with cold water. The residue, thus freed from the caustic alkalies, is transferred to a flask or bottle and treated with water. From this solution the more dilute ones are prepared as they are needed.

4. Dehydrated copper sulphate prepared from the pure salt by heating in an air-bath at 150° until the whole mass assumes a uniform light color. It is necessary to use pure copper sulphate for this purpose. The presence either of chlorides or of iron salts is not permissible, because of the solubility of cupric chloride and ferric sulphate in alcohol. It is not advisable to attempt to remove more than four of the five molecules of water of crystallisation, because of the danger of decomposing some of the salt at high temperatures. Such decomposition would result in the formation of free sulphuric acid, which would be extracted along with the boric acid by alcohol.

5. Absolute alcohol prepared by digesting for two or three days with dehydrated copper sulphate an alcohol which has previously been distilled over lime. The complete drying of the alcohol is important.

The Mode of Procedure.

If the boric acid is in solution, the liquid containing it is made slightly alkaline with caustic potassa, and evaporated on a water-bath in a porcelain dish having a width of about 100 millimeters. The volume of the solution should be reduced to 10 or 12 cubic centimeters. The separation of salts during evaporation will not interfere with subsequent operations. If the material containing the boric acid is not soluble in water, a silicate for example, a solution is effected by the method recommended by one of us for the decomposition of chrome iron.¹ About four grams of the purest solid potassium hydroxide are placed in a nickel crucible² and heated with a small flame until the fused mass becomes perfectly tranquil. The crucible is allowed to cool and the finely ground and weighed material spread over the surface of the solidified hydroxide. The whole is then heated for two hours to a temperature just sufficient to keep the hydroxide in a fused condition.

¹ This Journal 3, 163.

² A silver crucible is not to be recommended, because of the solubility of silver in potassium hydroxide.

During the decomposition the mass is frequently stirred with a stout platinum wire, which is allowed to remain in the crucible. This method of bringing the acid into a soluble condition is to be preferred to fusion with the alkaline carbonates, since it yields a mass from which everything soluble can be readily extracted by water. The crucible is placed on its side in a porcelain dish, treated with hot water, and the soluble separated from the insoluble matter by filtration and washing. The filtrate is then evaporated to the small volume previously mentioned. If the material thus decomposed contains iron, the contents of the crucible must be treated with not less than 400 cubic centimeters of water, and the dish in which the solution is made should be heated on the water-bath for a considerable time, with replacement from time to time of the evaporated water. Otherwise the separation of the iron may not be complete.

The solution of borate is treated, under proper covering to prevent loss by spattering, with a drop or two of tropaeolin solution, and then with the ordinary desk solution of sulphuric acid until a distinct and permanent acid reaction is obtained. The material on the under side of the cover is washed back into the dish with the least possible amount of water, and the slight excess of sulphuric acid carefully neutralised by means of very dilute caustic potassa. The solution of boric acid, which should not exceed 20 cubic centimeters in volume, is now thoroughly dried by slowly stirring into it the anhydrous copper sulphate, care being taken not to permit any considerable rise in temperature. The mass is afterwards pulverised with a pestle.

The extraction apparatus consists of a narrow Erlenmeyer flask having a capacity of about 150 cubic centimeters, and a straight chloride of calcium tube somewhat larger than is necessary to contain the mixture which is to be extracted. The narrow portion of the tube is plugged with cotton wool. To its lower end is attached, by means of rubber tubing, a small glass tube which reaches to the bottom of the flask when the stopper carrying the extraction tube is in position. The quantity of the dilute barium hydroxide solution which is equivalent to 25 cubic centimeters of the standard sulphuric acid, is run into the flask and the apparatus attached to the filter pump. This quantity of the hydroxide would weigh, if converted into carbonate, just 500 milligrams. During the filling of the extraction tube with the copper sulphate mixture,

the outside is occasionally tapped to render the material more compact.

The porcelain dish is washed with several small portions of absolute alcohol, which are then poured into the tube. When the whole of the copper sulphate has become wet with the alcohol the pump is shut off and the mass allowed to soak for fifteen minutes. Afterwards five other portions of absolute alcohol, of 15 cubic centimeters each, are poured into and slowly drawn through the tube, care being taken to allow each portion to filter through completely before another is added.

Finally, the excess of the barium hydroxide is precipitated by passing into it a current of carbon dioxide; the contents of the flask are transferred to a weighed platinum dish, evaporated to dryness, and heated to constant weight over a triple burner.

The quantity of boric anhydride is found by the following proportion:

Mol. weight of B_2O_3 —mol. weight of CO_3 : mol. weight of B_2O_3 :: weight found—theoretical weight of the barium as carbonate : weight of B_2O_3 found.

If the atomic weights of Clarke have been used throughout, the difference between the weight found and the calculated weight of the carbonate (500 milligrams) is to be multiplied by the number 2.697012; if those of Meyer and Seubert have been employed, this difference is to be multiplied by the number 2.701822.

The accuracy of the method was tested by determining the boric acid in pure borax glass (prepared by ourselves), in datholite from Bergen Hill, and in tourmaline from Pierrepont, N. Y.

We give the results below:

I. Borax Glass.

Measured portions of a standard solution were employed.

Theoretical percentage of B_2O_3 , 34.61. Found, 34.64, 34.58, 34.64, 34.57, 34.57.

Five determinations made by Mr. R. L. Henderson of this laboratory gave the following percentages of B_2O_3 in our borax glass, 34.60, 34.60, 34.59, 34.58, 34.59.

II. Datholite from Bergen Hill.

Theoretical percentage of B_2O_3 , 21.82. Found, 21.75, 21.68, 21.62, 21.65, 21.64. Mean, 21.67.

III. *Tourmaline from Pierrepont.*

This mineral was recently carefully analysed by Dr. Riggs.¹

Five determinations of the boric acid were made by ourselves, one by Mr. C. C. Blackshear and one by Mr. Henderson.

Percentage of B_2O_3 found by Dr. Riggs, 10.15, 10.00, 10.31; by ourselves, 10.03, 10.08, 10.11, 10.03, 10.13. Mean, 10.08. Found by Mr. Blackshear, 10.02; by Mr. Henderson, 10.12.

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PRELIMINARY NOTE ON THE CONSTITUTION OF
SODIUM ACETACETIC AND MALONIC ETHERS.

BY ARTHUR MICHAEL.

In the continuation of an investigation on the constitution of the sodium derivatives of acetacetic and malonic ethers, several observations were recently made that seem of sufficient importance to publish before the completion of the research.

The so-called acetyl-malonic ether was first made by Ehrlich and Conrad and Guthzeit, by the action of chlorcarbonic ether on sodium acetacetic ether; and lately, Lange has published a method for obtaining the substance from acetyl chloride and sodium malonic ether. It is theoretically very probable that the introduction of a negative group like carbethoxyl into acetacetic ether should increase the acid properties; but, to judge from the account Conrad and Guthzeit give of the substance, it hardly seems to be the case. This anomalous behavior of acetyl-malonic ether appeared to me to be a clue that might throw light on the much discussed question of the constitution of sodium acetacetic ether, and led me to re-investigate the subject. I find that the compound obtained from chlorcarbonic ether and sodium acetacetic ether is an entirely different substance from that obtained from acetyl chloride and sodium malonic ether. The first named substance is insoluble, and is not decomposed in the cold by strong alkaline solutions, and dissolves gradually in dilute alkalies under decomposition into acetone, alcohol, and carbonates. It can be recon-

¹ American Journal of Science 35, 45.

verted into acetacetic ether by means of sodium ethylate, but in this reaction a sodium product is not formed. Acetyl chloride and sodium malonic ether react to form two products, which were separated by fractionation in vacuum. They proved to be mono- and diacetyl malonic ethers. The mono-derivative boils in vacuum five degrees lower than its isomer obtained from acetacetic ether under the same conditions, and acts as a strong acid. It dissolves immediately in strong or dilute alkaline solutions, and even in solutions of alkaline carbonates, and is precipitated unchanged by addition of a mineral acid. Added to an alcoholic sodium ethylate solution, the white crystalline sodium derivative is immediately deposited.

In view of these remarkable results it seemed of interest to re-examine the action of chlorcarbonic ether on sodium malonic ether, as the methinyl-tricarboxylic ether of Conrad and Guthzeit does not form a sodium derivative, but is immediately decomposed by alcoholic sodium ethylate with the formation of sodium carbonate. These chemists employed a sodium malonic ether obtained by precipitating its alcohol solution with ether and drying in a vacuum, and then boiled the salt with a solution of chlorcarbonic ether in benzene. In my experiments the sodium derivative was made by the action of sodium on a dilute ethereal solution of malonic ether, and chlorcarbonic ether was added directly to the product. The substance obtained in this manner agrees in its physical properties very closely with those of the substance described by Conrad and Guthzeit, but differs materially from it in its chemical properties. It dissolves immediately in solutions of alkalis or alkali carbonates, and is precipitated unchanged by addition of a mineral acid; and the stable sodium derivative is formed at once when it comes in contact with alcoholic sodium ethylate.

The results with acetyl malonic ether seem to me to admit of but one plausible interpretation, namely, that sodium acetacetic ether has the constitution $\text{CH}_3-\text{CONa}-\text{CH}-\text{COOC}_2\text{H}_5$, although the free ether is undoubtedly represented by $\text{CH}_3-\text{CO}-\text{CH}_2-\text{COOC}_2\text{H}_5$. The product from chlorcarbonic and sodium acetacetic ethers is $\text{CH}_3-\text{COCOOC}_2\text{H}_5-\text{CH}-\text{COOC}_2\text{H}_5$, a view that explains the neutral properties and the products of decomposition by alkalis; while the substance from malonic ether is the real acetyl-malonic ether, and its constitution is therefore $\text{CH}_3-\text{CO}-\text{CH}(\text{COOC}_2\text{H}_5)_2$. The differences in the properties

of the methinyl-tricarboxylic ether of Conrad and Guthzeit, and the ether obtained by me, indicate that when sodium replaces hydrogen in malonic ether, the first phase of the reaction is the formation of $\text{CHNa}(\text{COOC}_2\text{H}_5)_2$; but, on heating, owing to the affinity of oxygen for sodium, this product passes over into the more stable form $\text{C} \begin{smallmatrix} \text{OC}_2\text{H}_5 \\ \text{ONa} \end{smallmatrix} - \text{CH} - \text{COOC}_2\text{H}_5$. According to

this view, the ether of Conrad and Guthzeit is $\text{C} \begin{smallmatrix} \text{OC}_2\text{H}_5 \\ \text{OCOOC}_2\text{H}_5 \end{smallmatrix} - \text{CH} - \text{COOC}_2\text{H}_5$, and my substance—it being made at a lower temperature—is the real methinyl-tricarboxylic ether, $\text{CH}(\text{COOC}_2\text{H}_5)_3$. Indeed, it is not improbable that in the replacement of hydrogen of acetacetic ether by sodium, the compound first formed is $\text{CH}_3 - \text{CO} - \text{CHNa} - \text{COOC}_2\text{H}_5$, but in this case a molecular rearrangement takes place at ordinary temperature, a view for which I shall endeavor to furnish an experimental basis.

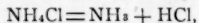
These experiments appear to me to open a wide field of discussion in regard to chemical reactions by substitution, and intermolecular changes due to the introduction of positive or negative radicals, that in the present note I can barely touch, but I shall return to the subject when the research is completed and published in full. The formation of homologues of higher carbon series by the action of alkyl haloids on sodium acetacetic ether must be explained by assuming an addition of the alkyl haloid to the sodium derivative and subsequent elimination of sodium haloid. How many of the so-called substitutions are in reality of a similar duplex nature? It can hardly be doubted that many of them represent but the final stage of an addition and subsequent elimination; a view that at least explains many facts at present difficultly or wholly unintelligible. Nor can it be doubted that cases similar to that described with acetacetic ether are uncommon, when hydrogen of an organic substance containing oxygen is replaced by a strongly positive atom. As an example, isatine may be mentioned, whose sodium derivative, according to this view, has the constitution $\text{C}_6\text{H}_5 \begin{smallmatrix} \text{N} \\ \text{CO} \end{smallmatrix} > \text{CONa}$, while the substance itself is represented by $\text{C}_6\text{H}_5 \begin{smallmatrix} \text{NH} \\ \text{CO} \end{smallmatrix} > \text{CO}$; an interpretation explaining the results obtained by v. Baeyer without the need of his pseudoform hypothesis.

REVIEWS AND REPORTS.

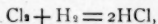
ETUDES DE DYNAMIQUE CHIMIQUE. Par J. H. van't Hoff. Amsterdam, 1884.

This book is so deserving of careful study and has apparently attracted so little attention in this country that a brief notice of it may not be out of place even now, more than three years after its publication. It is composed of an introductory chapter, a list of exact definitions of terms used, and four parts headed as follows: "The March of Chemical Transformation," "The Influence of Temperature," "Chemical Equilibrium," and "Affinity." Each of these parts is in turn subdivided into several heads.

In the introductory chapter the author calls attention to the broad generalisations reached by a study of physical constants as functions of chemical composition, and the far more limited applicability of results attained by a study of chemical action as a function of composition, taking as examples Brühl's and Menshutkin's work; and as results obtained by work similar to that of the latter chemist are not capable of general application on account of unknown factors due to secondary action and disturbing influence, he points out that the desired simple mathematical expression can be deduced only after a careful study of the "march of chemical transformation" step by step in such a way as to estimate and eliminate each disturbing factor. A large portion of the book is therefore devoted to a study of disturbing influences and methods of eliminating them. In the first part of the book it is shown that if but a single molecule reacts, as for example



the amount of change in unit time depends entirely on the quantity of the compound and the coefficient of velocity of the reaction. If more than one molecule reacts, for example,



other factors, such as dilution, must be taken into consideration, and the equation used to determine the coefficient of velocity must differ from that used if the reaction be unimolecular. This equation has been given a general form in which n represents the number of molecules that react, and if we have a reaction in which this number is unknown it becomes easy, if we can eliminate disturbing influences, to determine it from this formula. The disturbing influences known to exist are those exerted by the volume occupied by the reacting system, by changes in the medium or solvent brought about by the products of the reaction, by deposition of these products on the walls of the vessels, by the

shape and size of the vessels, and by atomic movements. The influence of volume may be eliminated by diluting the solution so that the volume occupied by a quantity of solution containing x of the substance is not less than the volume of x in the gaseous state. The influence exerted by the change in the menstruum may be determined by using solutions of different strengths and comparing their rate of change with that of solutions of the same strengths containing the products of the reaction. By moistening the walls of the vessels, and by selecting apparatus of proper shape and size, we can dispose of the third and fourth factors. The influence of atomic motion, which is exhibited by the peculiar behavior of some gases at a particular tension, may be eliminated by the use of a proper diluent. Each of these elements has been carefully studied by van't Hoff, and this portion of the book is particularly interesting. Contact action, induction, and the isomerism of maleic and fumaric acids have also been studied in detail by the author and the results of his work given.

The part entitled "The Influence of Temperature" shows a happy combination of experiment and of theoretical conceptions founded on the principles of thermodynamics. The formulæ deduced from theory and from experiment are found to agree remarkably well. A special chapter is devoted to a consideration of the temperature of ignition, which is defined as "that temperature at which the heat conducted away exactly equals that produced by chemical action."

In the chapters on "Chemical Equilibrium" van't Hoff makes use of the expression $xy \rightleftharpoons x + y$ to indicate that the reactions expressed by $xy = x + y$ and $x + y = xy$ occur simultaneously, and that equilibrium is established when equal amounts of xy and $x + y$ are formed in equal times. He compares chemical equilibrium with physical, and divides it into three forms: homogeneous, in which all the substances are either gaseous or liquid; heterogeneous, in which they are not all in the same physical state; and condensed, in which they are solid. He compares the first form ($N_2O_4 \rightleftharpoons 2NO$) with the deviations from the law of Boyle; the second ($NH_4S \rightleftharpoons NH_3 + H_2S$) with the state of equilibrium represented by a liquid in contact with its vapor; and the third (orthorhombic sulphur $\rightleftharpoons$ monoclinic sulphur) with a solid in contact with a liquid of the same composition (ice and water). The temperature at which the two condensed systems are in equilibrium, i. e. the temperature at which there is no apparent change in either system, is shown theoretically to be that at which the tension of their vapor is identical. In order still further to test the comparison, the effect of pressure on the temperature of transition of sulphur from the one form to the other was determined experimentally and found to agree perfectly with that calculated from the formula of the effect of pressure on the temperature of fusion. The conclusion reached by a mathematical study of the results obtained

by comparing physical and chemical equilibrium is, that if the state of equilibrium between two systems be changed by lowering the temperature, there is an increase in the amount of that system whose formation from the other is attended with the evolution of heat. From this it can be shown that while the so-called laws of Thomsen and Berthelot regarding maximum heat and maximum work hold good, in general, at ordinary temperatures, they are not true at high, nor are they laws even at ordinary temperatures, but only at absolute zero.

The chapters on "Affinity" deal with some very ingenious experiments upon measuring the attraction of solutions of salts for water and of salts for their water of crystallisation, and the work done in reactions which may be reversed by a change of temperature. That point at which the reaction is reversed is called the point of transition. It was found that the work performed in a chemical reaction depends on the heat evolved, the temperature of the point of transition, and the temperature at which the reaction takes place. A simple mathematical expression for this was deduced, and several interesting applications of this formula are pointed out in the book.

F. L.

SUR LA CONSTITUTION DE LA NAPHTALINE ET DE SES DÉRIVÉS. By F. Reverdin and E. Nœlting. Reprinted from the "Bulletin de la Société industrielle de Mulhouse," pp. 76, with twenty extensive tables. 8vo, paper, 6 marks. Mulhouse, Alsace: Veuve Bader & Cie., Printers and Editors.

In one of the early pages the authors use these words, which give a good idea of the scope of the book:

"The work which to-day we have the honor of presenting to you, and which shows the actual state of our knowledge of the naphthalene derivatives, is, for the most part, entirely new, having retained merely the general arrangement of material peculiar to our earlier work.

"We shall discuss at the outset the constitution of naphthalene, the number of its isomeric derivatives, and the methods for the determination of the chemical position. Further on we give, in the form of a series of tables, all the known derivatives, indicating in a few words the preparation, and giving the bibliography complete. With this arrangement it will be easy for any one who may wish to make a thorough study of certain classes of derivatives to refer directly, without loss of time, to the original memoirs. In many cases, from the preparation of a derivative we are already in a position to draw conclusions relative to its constitution, while in other cases its transformation into a derivative of known constitution serves to establish the same. In many cases the structure has not yet been determined with perfect precision, or may even be altogether doubtful. Where this is so, and in general where it appears

to us advantageous, we shall discuss the formulæ in notes annexed to each table."

Coming as this work does from the hands of those who not only occupy prominent places among the leaders in pure chemical research at the present time in Europe, but who at the same time, from their familiarity with the applications of the results of this research in the chemical industry, are able to speak with authority with reference to both sides of the subject, practical as well as theoretical, the book deserves to meet with a cordial reception both amongst those who would advance our knowledge in this fruitful and fascinating field, as well as at the hands of those who are engaged in the industrial applications of organic chemistry, to which latter class it cannot fail to prove of value. A. G. P.

NOTE.

Note on Opium Analysis.

In my paper on opium analysis (this Journal 8, 295), reference is made to the method of preparing the sample by kneading it on a slab of glass or wood. By the use of a small quantity of very fine dry starch, applied by means of a pepper-box with very small holes, this mixture is very much facilitated. The amount of starch needed is so small that it can make no difference in the percentage of morphia. Opiums containing 25 per cent. of water are easily manipulated with the use of starch, while without it they adhere badly to the hands and slab.

In comments which I have seen made upon my process of analysis this special point seems to have been overlooked—the presence of meconate of lime and other impurities in the crystallised morphia. These are not removed by the washing with the saturated solutions of morphia in alcohol and water, and the crystals therefore require the special treatment which I use in order to obtain the correct percentage of morphia present. If the extraction of the opium is done with the aid of lime, the meconate of lime is not present in the crystals, but the other impurities are to some extent, and the crystals still need purification before the final result is reached. But for reasons which I have given, the extraction with water alone is preferable to any other mode of treatment.

CHARLES M. STILLWELL.